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JOURNALS FROM WHICH ABSTRACTS ARE MADE.

Abbreviated Title.	Journal.
Chem. Rev. Fett- Harz-Ind.	Chemische Revue über die Fett- und Harz-Industrie.
Chem. Zeit.	Chemiker Zeitung.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Soc. Biol.	Comptes rendus des Séances de la Société de Biologie.
Exper. Stat. Record	Experiment Station Record.
Gazzetta	Gazzetta chimica italiana.
Geol. Mag.	Geological Magazine.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
Jahrb. Min. Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie. Beilage-Band.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Fed. Inst. Brewing.	Journal of the Federated Institutes of Brewing.
J. Geol.	Journal of Geology.
J. Hygiene	Journal of Hygiene.
J. Landw.	Journal für Landwirtschaft.
J. Med. Research	Journal of Medical Research.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. Physique	Journal de Physique.
J. pr. Chem.	Journal für praktische Chemie.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Roy. Soc. New South Wales.	Journal of the Royal Society of New South Wales.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
L'Orosi	L'Orosi.
Mem. Accad. Sci. Torino	Memorie della Reale Accademia delle Scienze di Torino.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Nuovo Cim.	Il Nuovo Cimento.
Öfver K. Vet.-Akad. Förh.	Öfversigt af Kongl. Vetenskaps-Akademiens Förhandlingar.
Pflüger's Archiv	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. Arch.	Pharmaceutical Archives.
Pharm. J.	Pharmaceutical Journal.
Pharm. Rev.	Pharmaceutical Review.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Proc. Amer. Physiol. Soc.	Proceedings of the American Physiological Society.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. Phil. Soc. Glasgow	Proceedings of the Glasgow Philosophical Society.
Proc. Physiol. Soc.	Proceedings of the Physiological Society.
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

ABBREVIATED TITLE.	JOURNAL.
Rev. intern. Falsi.	Revue internationale des Falsifications.
Rec. trav. chim.	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of the Royal Dublin Society.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
Sitzungsber. k. Akad. München.	Sitzungsberichte der königlich bayerischen Akademie der Wissenschaften in München.
Trans. Amer. Inst. Mining Eng.	Transactions of the American Institute of Mining Engineers.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Path. Soc.	Transactions of the Pathological Society.
Trans. Roy. Soc. Canada.	Transactions of the Royal Society of Canada.
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy.
U.S.A. Dept. Agric. Bull.	Bulletins of the Department of Agriculture, U.S.A.
U.S.A. Dept. Agric. Rep.	Reports of the Department of Agriculture, U.S.A.
Virchow's Archiv	Archiv für pathologische Anatomie und Physiologie und für klinische Medicin.
Wiss. Abhandl. Phys.-Tech. Reichsanstalt.	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
Zeit. anal. Chem.	Zeitschrift für analytische Chemie.
Zeit. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeit. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeit. Biol.	Zeitschrift für Biologie.
Zeit. Elektrochem.	Zeitschrift für Elektrochemie.
Zeit. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeit. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeit. öffentl. Chem.	Hoppe-Seyler's Zeitschrift für öffentliche Chemie.
Zeit. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeit. physiol. Chem.	Zeitschrift für physiologische Chemie.
Zeit. prakt. Geol.	Zeitschrift für praktische Geologie.
Zeit. Ver. deut. Zuckerind.	Zeitschrift des Vereins der deutschen Zucker-Industrie.
Zeit. Zuckerind. Böhm.	Zeitschrift für Zuckerindustrie in Böhmen.

JOURNAL

OF

THE CHEMICAL SOCIETY.

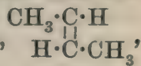
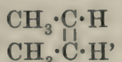
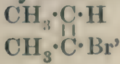
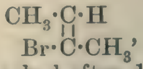
ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

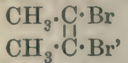
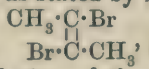
Configuration of Fatty Compounds. By Pavel Iw. Petrenko-Kritschenko (*J. pr. Chem.*, 1900, [ii], 315—320).—A continuation of the controversy between the author (Abstr., 1900, i, 421) and Krafft (*ibid.*, 577). R. H. P.

The Geometrically Isomeric Symmetrical Dimethylethylenes (ψ-Butylenes), their Bromo-derivatives, and β-Bromomonocarboxylic acids. By Johannes Wislicenus (*Annalen*, 1900, **313**, 207—209).—An introduction to the following two papers, of which the first comprises revision of a previous paper on the same subject (Hölz, Abstr., 1889, 575). M. O. F.

Derivatives of ψ-Butylene Dibromide and Crotonylene Hydrobromide. By Johannes Wislicenus and Paul Schmidt (*Annalen*, 1900, **313**, 210—228).—The authors have prepared considerable quantities of ψ-butylene by the method of Le Bel and Greene, which consists in allowing *iso*butyl alcohol to drop on fused zinc chloride, and absorbing the *iso*butylene with sulphuric acid; the hydrocarbon thus obtained is a mixture of the centro-symmetrical ψ-butylene,  $\begin{array}{c}CH_3\cdot C\cdot H\\ \|\\ H\cdot C\cdot CH_3\end{array}$, with the plano-symmetrical hydrocarbon,  $\begin{array}{c}CH_3\cdot C\cdot H\\ \|\\ CH_3\cdot C\cdot H\end{array}$, in the proportion 1 : 2. The dibromide obtained when this mixture combines with bromine is separable into two fractions, of which that having the higher boiling point (158—159°), when decomposed with potassium hydroxide (1 mol.), yields plano-symmetrical bromo-ψ-butylene (?),  $\begin{matrix}CH_3\cdot C\cdot H\\ \|\\ CH_3\cdot C\cdot Br\end{matrix}$, in larger amount than the lower fraction (157—158°), but in both fractions the centro-symmetrical isomeride,  $\begin{matrix}CH_3\cdot C\cdot H\\ \|\\ Br\cdot C\cdot CH_3\end{matrix}$, preponderates; only 15 per cent. of the latter is attacked after 1 hour with 15 per cent. alcoholic potash, whereas the plano-symmetrical derivative is thereby completely resolved into crotonylene. In other words, of the greater part of the ψ-butylene dibromide, one-third is converted into the plano-symmetrical bromo-ψ-butylene, the remaining two-thirds yielding the centro-symmetrical modification.

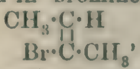
The boiling point of the centro-symmetrical bromo-ψ-butylene is certainly not lower than 93—94°, but the presence of hydrogen bromide induces transformation into the plano-symmetrical modification; this change takes place at the ordinary temperature, and is accelerated by sunlight, and the boiling point therefore becomes depressed. The plano-symmetrical modification has an agreeable odour when freshly prepared, boils at 83·5—84·5°, and has a sp. gr. 1·3152 at 26°/4°; when exposed to light, it acquires a disagreeable odour, and, hydrogen bromide being eliminated, undergoes transformation into the centro-symmetrical modification, but not to so great an extent as in the converse case.

Ethylacetylene [butinene], CEt⁝CH, is a colourless, very limpid liquid which boils at 17—18°; it yields explosive precipitates with ammoniacal silver chloride and alcoholic silver nitrate solutions. Dimethylacetylene or crotonylene, CMe⁝CMe, boils at 27·2—27·6°.

Plano-symmetrical crotonylene dibromide,  $\begin{matrix}CH_3\cdot C\cdot Br\\ \|\\ CH_3\cdot C\cdot Br\end{matrix}$, boils at 146—146·5° under 740 mm. pressure; excess of bromine converts it into crotonylene tetrabromide, $CBr_2Me\cdot CBr_2Me$, which melts at 243°, and not at 230° as stated by Faworsky. Centro-symmetrical crotonylene dibromide,  $\begin{matrix}CH_3\cdot C\cdot Br\\ \|\\ Br\cdot C\cdot CH_3\end{matrix}$, prepared by the action of zinc dust on the alcoholic solution of the tetrabromide, boils at 149—150°.

M. O. F.

Geometrically Isomeric Symmetrical Dimethylethylenes [ψ-Butylenes] from Tiglic and Angelic Acids. By JOHANNES WISLICENUS, HENRY PAUL TALBOT, and MARTIN HENZE (*Annalen*, 1900, **313**, 228—242).—The hydriodides of tiglic and angelic acids (E. Schmidt, Abstr., 1881, 1126) are best prepared in chloroform solution, the former crystallising from light petroleum in colourless leaflets which melt at 86·5—87°; the hydriodide of angelic acid is more readily soluble than the isomeride melting at 59·5—60·5°, and undergoes transformation into the latter on repeated recrystallisation.

When the hydriodide of tiglic acid is treated with sodium carbonate, and the hydrocarbon which is generated collected in bromine, the dibromide which is formed yields bromo-ψ-butylene,  $\begin{matrix}CH_3\cdot C\cdot H\\ \|\\ Br\cdot C\cdot CH_3\end{matrix}$, on treatment with alcoholic potash; when submitted to the same series of changes, the hydriodide of angelic acid yields crotonylene hydrobromide, $\begin{array}{l}CH_3\cdot C\cdot H\\ \qquad \| \\ CH_3\cdot C\cdot Br\end{array}$. The former substance, which must have arisen from plano-symmetrical ψ-butylene, $\begin{array}{l}CH_3\cdot C\cdot H\\ \qquad \| \\ CH_3\cdot C\cdot H\end{array}$, boils at 93·5°, and is identical with the substance previously regarded as centro-symmetrical bromo-ψ-butylene (see preceding abstract), whilst crotonylene hydrobromide, boiling at 85—86°, is derived from centro-symmetrical ψ-butylene.

M. O. F.

Action of Bromine on Trimethylene under different Conditions. By Gabriel Gustavson (*J. pr. Chem.*, 1900, [ii], **62**, 273—295).—A detailed description of researches, of which a summary has already appeared (Abstr., 1900, i, 535).

R. H. P.

Decomposition of Iodoform in Chloroform Solution. By M. C. Schuyten (*Chem. Centr.*, 1900, ii, 1007; from *Bull. Acad. roy. Belg.*, [iii], **38**, 625—639).—(1) In solutions of the same concentration, at the same temperature and with free access to air, the less the quantity of iodoform the greater the proportion decomposed. (2) In solutions of different concentrations, the greatest decomposition occurs in the most dilute. (3) The higher the temperature, the greater the decomposition. (4) As the volume of air in contact with the solution is increased, the amount of decomposition also increases. When air is excluded and the solution exposed to light, the greater the intensity of the light, the greater the decomposition effected. Solutions may be kept in the dark for a week without change, for under such conditions only a rise of temperature causes a separation of iodine. When a solution which has been exposed to light until iodine has begun to be liberated is placed in the dark, the decomposition still proceeds. A series of experiments, in which solutions were allowed to remain in contact with less air than that theoretically required for the separation of the whole of the iodine, showed that, nevertheless, the iodoform would in time be completely decomposed.

E. W. W.

***iso*Nitroso-compounds.** By Arnold F. Holleman (*Ber.*, 1900, **33**, 2913—2914).—A question of priority (compare Abstr., 1896, i, 148; 1897, i, 599; Hantzsch and Schultze, Abstr., 1896, i, 353; Hantzsch and Veit, Abstr., 1899, i, 401; and Hantzsch, *Ber.*, 1900, **33**, 2542).

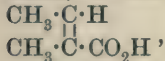
A. H.

Acetals of Polyhydric Alcohols. By Marcel Delépine (*Compt. rend.*, 1900, **131**, 745—747).—The diacetal of *i*-erythritol, which has not hitherto been described, is obtained by adding acetaldehyde to a cooled solution of *i*-erythritol in hydrochloric acid; it is soluble in chloroform, alcohol, or water, from which it crystallises in prismatic needles, melts at 94·5—95°, boils at 201°, and sublimes below the latter temperature. The following thermochemical data were obtained:

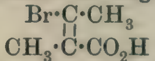
	Molecular heat of combustion.		
	Constant volume.	Constant pressure.	Molecular heat of formation.
Glycol formal	409·4 Cal.	409·6 Cal.	80·3 Cal.
,, acetal...........	558·24	558·8	94·4
i-Erythritol diformal..	744·3	744·6	166·2
,, diacetal...	1048·0	1048·8	188·6
d-Mannitol triformal..	1083·22	1083·5	248·2
,, triacetal ..	1536·91	1538·1	283·5

These results show that the heat of formation increases with the number of hydroxyl groups in the alcohol, and is greater for the acetals than for the corresponding formals, conclusions which are in accord with the known facts respecting the relative stability of the compounds. N. L.

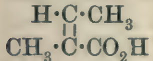
Geometrically Isomeric α-Methyl-β-crotonic Acids. By JOHANNES WISLICENUS and MARTIN HENZE (*Annalen*, 1900, **313**, 243—250).—According to theoretical views expressed by J. Wislicenus, it was to be expected that the dibromide of angelic acid,


$\begin{matrix}CH_3\cdot C\cdot H\\ \Vert\\ CH_3\cdot C\cdot CO_2H\end{matrix}$

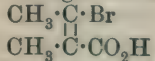
, would yield β-bromotiglic acid,


$\begin{matrix}Br\cdot C\cdot CH_3\\ \Vert\\ CH_3\cdot C\cdot CO_2H\end{matrix}$

, on treatment with alcoholic potash, and that the dibromide of tiglic acid,


$\begin{matrix}H\cdot C\cdot CH_3\\ \Vert\\ CH_3\cdot C\cdot CO_2H\end{matrix}$

, would give rise to β-bromoangelic acid,


$\begin{matrix}CH_3\cdot C\cdot Br\\ \Vert\\ CH_3\cdot C\cdot CO_2H\end{matrix}$

; of these, it might be anticipated that the former would be more stable than the latter, the salts of which should easily break up into metallic bromide, carbon dioxide, and crotonylene (dimethylacetylene). These anticipations have been verified.

β-Bromoangelic acid crystallises from light petroleum in rosette-like aggregates of needles melting at 94—95°; the sodium salt decomposes in aqueous solution, yielding crotonylene.

β-Bromotiglic acid crystallises from light petroleum in large, monoclinic prisms and melts at 100—101°. M. O. F.

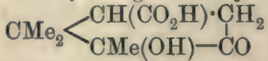
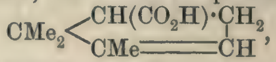
Direct Nitration in the Fatty Series. By LOUIS BOUVEAULT and A. WAHL (*Compt. rend.*, 1900, **131**, 687—689).—The action of well cooled fuming nitric acid on ethyl dimethylacrylate yields *ethyl nitrodimethylacrylate*, a pale yellow liquid of sp. gr. 1·1384 at 0°, with a peculiar piquant and somewhat disagreeable odour. It boils without decomposing at about 220° under atmospheric pressure. When dissolved in benzene, its molecular weight is normal. It is insoluble in water and acid, and dissolves slowly in cold solutions of alkali hydroxides, but is dissolved and decomposed on heating. Ordinary reducing agents have no action on it. When treated with alcoholic potash, it yields a potassium salt, $C_7H_{10}O_4NK$, from which, by the action of hydrochloric acid, an isomeric ethyl β-nitrodimethylacrylate is obtained as a colourless liquid which boils at 104—105° under 170 mm. pressure, has a sp. gr. 1·1279 at 0°/0°, and dissolves at once in cold solutions of alkali hydroxides. C. H. B.

Constitution of the Nitro-derivatives of Ethyl Dimethylacrylate. Ethyl Nitroacetate. By LOUIS BOUVEAULT and A. WAHL (*Compt. rend.*, 1900, **131**, 748—750).—Ethyl dimethylacrylate is converted by the action of fuming nitric acid into ethyl α-nitrodimethylacrylate which, when treated with alcoholic potash, yields the potassium salt of the isomeric ethyl β-nitrodimethylacrylate. When an ethereal solution of ethyl β-nitrodimethylacrylate is saturated with dry ammonia, an unstable ammonium salt is formed, whereas the α-ester, when similarly treated, is converted into acetone and an ammonium compound, $C_4H_{10}O_4N_2$, from which hydrochloric acid liberates ethyl nitroacetate. This ester is thus obtained as a colourless liquid boiling at 105—107° under 25 mm. pressure, and having a sp. gr. 1·226 at 0°/0°, which appears to be isomeric with the ethyl nitroacetate described by de Forcrand as boiling at 151—152°. It is concluded from these results that ethyl α- and β-nitrodimethylacrylates have the constitutions $CMe_2{:}C(NO_2){\cdot}CO_2Et$ and $CH_2{:}CMe{\cdot}CH(NO_2){\cdot}CO_2Et$ respectively. N. L.

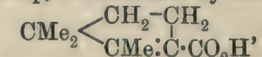
Oxidation of Higher Unsaturated Fatty Acids with Sulphuric Acid and Ammonium Persulphate. By ALEXIUS ALBITZKY (*Ber.*, 1900, **33**, 2909—2910).—When oxidised with a mixture of sulphuric acid and ammonium persulphate, oleic, elaidic, erucic, and brassic acids give the dihydroxy-acids which have already been described as oxidation products when alkaline permanganate was used (compare Abstr., 1899, i, 862). T. M. L.

The two Campholytic Acids and Lauronolic Acid. By FERDINAND TIEMANN (*Ber.*, 1900, **33**, 2935—2952).—[With MAX KERSCHBAUM and HERMANN TIGGES].—Liquid campholytic acid, $C_9H_{14}O_2$, first obtained by Walker as a product of the electrolysis of sodium orthoethyl camphorate (Trans., 1893, **63**, 498), and subsequently by Noyes from β-camphoramic acid, has been distinguished by the latter investigator as *cis-trans*-campholytic acid, the solid isomeride originally called *iso*lauronolic acid being regarded as the *cis*-modification. By way of avoiding confusion, the authors refer to these compounds in the present paper as α- and β-campholytic acids respectively.

α-Campholytic acid, $C_9H_{14}O_2$, obtained from β-camphoramic acid by oxidation with sodium hypobromite, and subsequent treatment of the resulting aminodihydrocampholytic acid with nitrous acid, is separated from the accompanying hydroxydihydrocampholytic acid (Noyes, Abstr., 1895, i, 295) by agitation with light petroleum, which removes also the lactone, $C_9H_{14}O_2$; it is a colourless oil which becomes yellow on standing, boils at 126—128°, 139—140°, and 235—236° under pressures of 8 mm., 15 mm., and 760 mm. respectively, has a sp. gr. 1·014 at 17°, n_D 1·47116, and $[\alpha]_D$ -73 at 45°. *Campholytolactone*, $C_9H_{14}O_2$, distils readily in steam, forming a camphor-like mass with a peculiar odour; it melts at 115—116°, and boils at 105—108°, and 228—230° under pressures of 8 mm., and 760 mm. respectively. The *hydroxy-acid*, $C_9H_{16}O_3$, obtained by hydrolysing the lactone with baryta, crystallises from ethyl acetate in broad needles melting at 121°; in every respect but melting point it resembles hydroxydihydrocampholytic acid, passing readily into *iso*lauronolic acid on treatment with acids, and the authors consider it probable that the relation between the two substances is one of geometrical isomerism, and that the hydroxyl group occupies the γ- instead of the β-position, as supposed by Noyes.

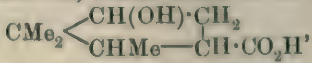
When α-campholytic acid is oxidised with alkaline potassium permanganate at 0°, two crystalline substances are produced, of which the *acid*, $C_9H_{14}O_4$, which crystallises from ethyl acetate in prisms melting and decomposing at 192°, is regarded by the authors as the hydroxyketonic compound,  $CMe_2<\begin{matrix}CH(CO_2H)\cdot CH_2\\ CMe(OH)-CO\end{matrix}$; this acid yields no precipitate with copper acetate, whilst *dihydroxydihydrocampholytic acid*, $C_9H_{16}O_4$, which crystallises from ethyl acetate in octahedra, and melts at 158°, forms a crystalline copper salt. Oxidation with dilute nitric acid resolves α-campholytic acid into dimethyltricarballylic and dimethylglutaric acids; the authors represent its constitution therefore by the formula  $CMe_2<\begin{matrix}CH(CO_2H)\cdot CH_2\\ CMe=\!=\!=CH\end{matrix}$, which accords with the production of dimethyltricarballylic acid, regarding the dimethylglutaric acid as due to the *iso*lauronolic acid formed by molecular transformation preceding oxidation. β-Campholytic (*iso*lauronolic) acid, when oxidised with potassium permanganate, yields iso*campholytonic* (*iso*lauronic) *acid*, along with dimethylhexanonic and dimethylglutaric acids, whilst dilute nitric acid produces dimethylglutaric and dimethylsuccinic acids, but no trace of dimethyltricarballylic acid.

In consequence of these observations, the authors maintain that α-campholytic and *iso*lauronolic acids are not geometrical isomerides, and that during the transformation into *iso*lauronolic acid the change which α-campholytic acid undergoes is very profound, involving migration of the carboxyl group, as indicated by the formula,



$$CMe_2<\begin{matrix}CH_2-CH_2\\ CMe{:}C\cdot CO_2H\end{matrix}$$

for *iso*lauronolic acid.

In the way that β-camphoramic acid yields campholytic acid, lauronolic acid is obtained from α-camphoramic acid, and because it differs slightly from the acid produced by Aschan's modification of the method of Fittig and Woringer, which depends on the decomposition of bromocamphoric anhydride with alkali carbonate, has been called γ-lauronolic acid by Noyes. γ-Lauronolic acid, which is identical with the *allo*campholytic acid of Walker and Henderson (Trans., 1895, **67**, 341), is a pale yellow oil which boils at 130—132·5° under 12 mm. pressure, has a sp. gr. 1·0177, n_D 1·47155, and $[\alpha]_D$ +145·9° at 20°; as, however, this value is not always observed, but varies between 118° and 146°, it is possible that the acid from this source is a mixture of two modifications having different optical properties. The acid from camphanic acid has α_D varying between 110° and 188°, bromocamphoric anhydride yielding lauronolic acid with the constant rotation +199° in a 1 dcm. tube. Boiling acids convert lauronolic acid into campholactone, which melts at 50° and yields hydroxydihydrolauronolic acid,  $CMe_2<\begin{matrix}CH(OH)\cdot CH_2\\ CHMe-CH\cdot CO_2H\end{matrix}$, on hydrolysis; this crystallises from water in prisms melting at

144—145°, and when boiled in a vacuum yields campholactone, water, and an acid which melts at 189°. *Dibromodihydrolauronolic acid*, $C_9H_{14}O_2Br_2$, produced in association with the bromolactone when the calculated amount of bromine acts on γ-lauronolic acid in chloroform solution, crystallises from benzene and melts at 185°; the solution in dilute sodium carbonate rapidly deposits bromocampholactone, which melts at 187°. Laurolene (compare Walker and Henderson, Trans., 1896, **69**, 750) boils at 121—122°, has sp. gr. 0·8008 at 17·5°, n_D 1·44376, and a_D +19·9° in a 1 dcm. tube.

When lauronolic acid is oxidised with potassium permanganate, a ketone and a dihydroxy-acid are produced. *Laurenone*, $C_8H_{12}O$, the ketone, is optically inactive, and forms a colourless liquid with a nutty odour; it boils at 92—95° under 16 mm. pressure, has a sp. gr. 0·9572 at 12·5°, and n_D 1·48535. The *oxime*, $C_8H_{13}ON$, crystallises from petroleum in prisms, and melts at 105—107°; the *hydroxylamino-oxime*, $C_8H_{16}O_2N_2$, forms white crystals melting at 159°, and when boiled with water and mercuric oxide develops a blue coloration, indicating the tertiary character of the hydroxylamine group.

Dihydroxydihydrolauronolic acid, $C_9H_{16}O_4$, crystallises from water and melts at 153—154°; the *copper* salt is sparingly soluble.

M. O. F.

Oxalates. By GRÉGOIRE N. WYROUBOFF (*Chem. Centr.*, 1900, ii, 839—843; from *Bull. Soc. franç. Min.*, **23**, 65—141).—A detailed account of the double oxalates, $M'''_2(C_2O_4)_6M'_6$ where M''' = Al, Cr, Fe and M' = NH_4, K, Rb, Tl, Na, Li. Some salts are also described containing two of the alkali metals; most of these come under the general formula given, but a few are of the more complex type $M'''_8(C_2O_4)_{24}M'_{24}$. The crystallography of the salts is described.

E. W. W.

Action of Ammonia and Amines on Halogen-succinic Acids. By OSKAR LUTZ (*Chem. Centr.*, 1900, ii, 1009—1014; from *Diss. Rostock*, 1899).—d-*β-Malamic acid*, $CO_2H\cdot CH(OH)\cdot CH_2\cdot CO\cdot NH_2$, prepared by the action of ammonia on *l*-bromosuccinic acid, melts at 149°, has a sp. gr. 1·577 at 18°/4° and $[a]_D$ 9·70° in aqueous solution; 100 parts of water dissolve 7·52 of the acid at 18°. The *silver* salt, $C_4H_6O_4NAg$, forms lustrous leaflets and has $[a]_D$ +16·4° in aqueous solution and dissociation coefficient $K = 0·0286$. l-*β-Malamic acid* is prepared from *d*-chlorosuccinic acid, from *l*-malamide, or from methyl hydrogen malate (see later); it melts at 148·5—149°, has a sp. gr. 1·576 at 18°/4°, $[a]_D$ −9·33° in aqueous solution, and, like the dextro-acid, is readily hydrolysed by bases forming the corresponding malic acid. The *sodium* salt has $[a]_D$ −27·32° in aqueous solution. i-*β-Malamic acid* is prepared from *i*-bromosuccinic acid, or by mixing equal quantities of the dextro- and lævo-acids, and may be separated into its components by means of the cinchonine salts; it melts at 148°, is almost insoluble in methyl or ethyl alcohol and insoluble in ether, and has a sp. gr. 1·526 at 18°/4°; 100 parts of water dissolve 4·02 of acid at 18°. d-*β-Cinchonine malamate* melts at 165—167°, and is less soluble in water than the corresponding lævo-compound. i-β-Malamic acid is not identical with Curtius and

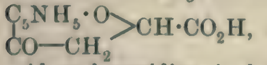
Koch's acid (Abstr., 1887, 34), and attempts to obtain the latter by the method described by these authors failed, *i*-β-malic acid monamide being formed; hence a portion of the ester of diazosuccinamic acid must have the composition $CO_2R\cdot CN_2\cdot CH_2\cdot CONH_2$. Although the salts of β-malamic acid are not affected by heating in aqueous solution, the rotatory power of an aqueous solution of the acid increases on heating, whilst the acidity as determined by barium hydroxide solution decreases. Walden's rule (Abstr., 1896, i, 553) that of optical isomerides the one of higher melting point has a less solubility and a less molecular volume does not hold in the case of the β-malamic acids.

Benzylamine d-*β-benzylmalamate*,

$$C_7H_7\cdot NH_3\cdot CO_2\cdot CH(OH)\cdot CH_2\cdot CO\cdot NH\cdot C_7H_7,$$

obtained by the action of benzylamine on *l*-bromosuccinic acid dissolved in methyl alcohol, melts at 152—153°, is soluble in water or methyl alcohol, and practically insoluble in ether, has $[\alpha]_D$ $+31\cdot43°$ in methyl alcohol solution at 20° and $+28\cdot0°$ in aqueous solution. d-*β-Benzylmalamic acid*, $CO_2H\cdot CH(OH)\cdot CH_2\cdot CO\cdot NH\cdot C_7H_7$, obtained by the action of hydrochloric acid on the benzylamine salt, crystallises from light petroleum in lustrous leaflets, melts at 130—131°, is easily soluble in methyl or ethyl alcohol and insoluble in ether, has a sp. gr. 1·347 at 18°/4° and $[\alpha]_D$ $+13\cdot6°$ in methyl alcohol solution; 100 parts of water dissolve 1·36 of the acid at 18°. The acid may also be prepared directly in aqueous solution. The *sodium* salt has $[\alpha]_D$ $+33\cdot8°$ in aqueous solution. l-*β-Benzylamine benzylmalamate*, prepared from *d*-chlorosuccinic acid, has $[\alpha]_D$ $-31\cdot33°$ in methyl alcohol solution. l-*β-Benzylmalamic acid* melts at 130—131°, has $[\alpha]_D$ $-13\cdot8°$ in methyl alcohol solution, and sp. gr. 1·349 at 18°/4°; 100 parts of water dissolve 1·39 of the acid at 18°. i-*β-Benzylamine benzylmalamate*, obtained from *i*-bromosuccinic acid, melts at 149°, is soluble in water or methyl alcohol, insoluble in ether, and forms a *silver* salt, $C_{11}H_{12}NO_4Ag$. *i*-β-Benzylmalamic acid melts at 131°, and has a sp. gr. 1·360 at 18°/4°; 100 parts of water dissolve 0·820 of the acid at 18°. The acid may also be prepared by mixing the dextro- and lævo-acids, but in this case contraction does not occur (Liebisch, *Annalen*, 1895, **286**, 140).

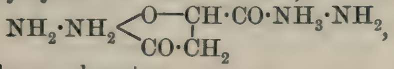
By the action of tribenzylamine on halogen succinic acids only inactive products are formed, but pyridine yields active compounds. The latter are extremely weak acids, and separate as such from alcoholic solutions since they do not combine with pyridine. Unlike the analogous triethylamine and *iso*butylamine compounds (Abstr., 1898, i, 127), the pyridine compounds, when hydrolysed by means of warm potassium hydroxide solution or hydrochloric acid, do not yield malic acid. d-*Pyridineaminosuccinic acid* [d-*Pyridiniummalic acid*],



$\left.\begin{array}{l}C_5NH_5\cdot O\\ |\\ CO—CH_2\end{array}\right>CH\cdot CO_2H$, obtained when a mixture of *l*-bromosuccinic acid and pyridine is left for two months, melts and decomposes at 190—191°, is easily soluble in hot water, alkalis or acids, insoluble in alcohol or ether, has a sp. gr. 1·435 at 18°/4°, and $[\alpha]_D$ $+10\cdot6°$ when dissolved in 1 part of $2N$ hydrochloric acid solution and 4 parts of water; 100 parts of water dissolve 1·67 parts at 18°. The *sodium* salt has $[\alpha]_D$ +17·01 in aqueous solution. The *silver* salt is very sensitive to the action of light. l-*β-Pyridiniummalic acid*, prepared by leaving a mixture of pyridine and *d*-chlorosuccinic acid for four months, melts at 190—191°, has a sp. gr. 1·435 at 18°/4°, and $[\alpha]_D$ $-10·5°$ when dissolved in 2*N* hydrochloric acid and 4 parts of water; 100 parts of water dissolve 1·435 of the acid at 18°. i-*β-Pyridiniummalic acid*, obtained from *i*-bromosuccinic acid, melts at 186—187°, and has a sp. gr. 1·435 at 18°/4°; 100 parts of water dissolve 1·70 of the acid at 18°.

By the action of dibenzylamine on *l*-bromosuccinic acid, a product consisting of at least two isomerides is obtained, one of which is *β*-dibenzylmalamic acid, $CO_2H\cdot CH(OH)\cdot CH_2\cdot CO\cdot N(C_7H_7)_2$. Benzylmethylamine acts on *l*-bromosuccinic acid in a similar way.

By the action of hydrazine on *l*-bromosuccinic acid, a *compound* which is probably hydrazineaminosuccinate,



$$NH_2\cdot NH_2 < \begin{matrix} O—CH\cdot CO\cdot NH_3\cdot NH_2 \\ CO\cdot CH_2 \end{matrix},$$

or hydrazinehydrazomalamate,

$$NH_2\cdot NH_3\cdot CO_2\cdot CH(OH)\cdot CH_2\cdot CO\cdot NH\cdot NH_2,$$

is formed; it is easily soluble in water, insoluble in alcohol or ether, has $[\alpha]_D$ +34·83° in aqueous solution and when hydrolysed yields *d*-malic acid. Malic acid diphenylhydrazide,

$$N_2H_2Ph\cdot CO\cdot CH(OH)\cdot CH_2\cdot CO\cdot N_2H_2Ph,$$

prepared by the action of phenylhydrazine (3 mols.) on *l*-bromosuccinic acid (1 mol.) in alcoholic solution, melts at 214° and is identical with the compound obtained by the action of phenylhydrazine on ethyl malate and with Bülow's hydrazide (Abstr., 1887, 138) which melts at 213°; 100 c.c. of absolute alcohol dissolve 0·0052 of this compound and 0·0070 of Bülow's hydrazide at 18°.

β-Malamic acid may also be obtained by partially hydrolysing malamide with hydrochloric acid or potassium hydroxide solution or by the action of ammonia on methyl hydrogen malate or ethyl malate. The increase in conductivity in the case of the sodium salt, $\mu_{1024}-\mu_{32}=9·42$, indicates the monobasic character of the acid. *Methyl* d-*β-malamate*, $CO_2Me\cdot CH(OH)\cdot CH_2\cdot CO\cdot NH_2$, melts at 75—76°, is soluble in hot methyl alcohol and has $[\alpha]_D$ +12·7° in methyl alcohol solution. d-*Malamide*, prepared from the preceding ester, melts at 156—157°, has $[\alpha]_D$ +37·9° in aqueous solution. *Methyl* l-*β-malamate* melts at 75—76°, and has $[\alpha]_D$ $-12·5°$ in methyl alcohol solution. l-*Malamide* melts at 156—157° and has $[\alpha]_D$ $-37·9°$ in aqueous solution. *Methyl* i-*β-malamate* melts at 113°. *i*-Malamide melts at 163—164°.

Methyl l-*α-malamate*, $CO_2Me\cdot CH_2\cdot CH(OH)\cdot CO\cdot NH_2$, prepared by the action of dry ammonia on methyl malate, melts at 66—67°, is insoluble in ether and has $[\alpha]_D$ $-48·48°$ in methyl alcohol solution. Ethyl *l*-*α*-malamate (Pasteur, *Ann. Chim. Phys.*, 1853, [iii], **38**, 457) melts at 102—103°, is soluble in alcohol but insoluble in ether and has $[\alpha]_D$ $-42·0°$ in methyl alcohol solution. Malamide may be prepared from the esters of *α*-malamic acid.

The ester prepared from *β*-malamic acid and that obtained from a dialkyl ester of malic acid yield the same diamide. The diamide

$NH_2 \cdot CO \cdot CH(OH) \cdot CH_2 \cdot CO \cdot NH(C_7H_7)$, prepared by the action of benzylamine on the ester of α-malamic acid, is identical with the compound prepared by the action of alcoholic ammonia on the ester of β-benzylmalamic acid but not with the mixed amide obtained by the action of ammonia on the methyl ester prepared from β-malamic acid by means of the silver salt. *Methyl* d-*β-benzylmalamate* melts at 105°, is easily soluble in hot alcohol, insoluble in ether and has $[\alpha]_D$ $+12 \cdot 8°$ in methyl alcohol solution.

d-*β-Benzylmalamide*, prepared by the action of alcoholic ammonia on the corresponding ester, melts at 131°, is easily soluble in methyl or ethyl alcohol or hot water, insoluble in ether, and has $[\alpha]_D$ $+42 \cdot 40°$ in methyl alcohol solution. l-*β-Benzylmalamide*, obtained by the action of benzylamine on methyl *l*-α-malamate, melts at 131—132° and has $[\alpha]_D$ $-42 \cdot 62°$ in methyl alcohol solution. d-*α-Benzylmalamide*, obtained by the action of benzylamine on methyl *d*-β-malamate in methyl alcohol solution, melts at 125—126° and has $[\alpha]_D$ $+44 \cdot 56°$ in methyl alcohol solution. d-*α-Benzylallylmalamide*,

$$C_3H_5 \cdot NH \cdot CO \cdot CH(OH) \cdot CH_2 \cdot CO \cdot NH \cdot C_7H_7,$$

prepared from allylamine and methyl *d*-β-benzylmalamate, crystallises in needles, melts at 107—108°, is easily soluble in methyl or ethyl alcohol, and has $[\alpha]_D$ $+41 \cdot 04°$ in methyl alcohol solution. d-*α-Allylmalamide*, $C_3H_5 \cdot NH \cdot CO \cdot CH(OH) \cdot CH_2 \cdot CO \cdot NH_2$, obtained from allylamine and methyl *d*-β-malamate, melts at 124—125° and has $[\alpha]_D$ $+49 \cdot 68°$ in methyl alcohol solution. l-*β-Allylmalamide*,

$$NH_2 \cdot CO \cdot CH(OH) \cdot CH_2 \cdot CO \cdot NH \cdot C_3H_5,$$

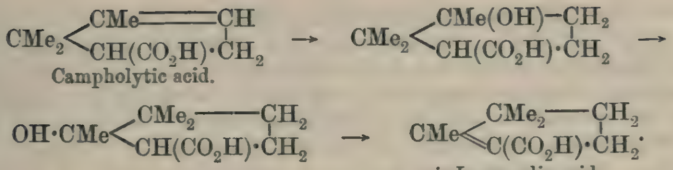
prepared from methyl *l*-α-malamate and allylamine in alcoholic solution, melts at 134—135°, and has $[\alpha]_D$ $-52 \cdot 25°$ in methyl alcohol solution. d-*β-Benzylmethylmalamide*,

$$NHMe \cdot CO \cdot CH(OH) \cdot CH_2 \cdot CO \cdot NH \cdot C_7H_7,$$

obtained from methyl *d*-β-benzylmalamate and methylamine in alcoholic solution, melts at 128° and has $[\alpha]_D$ $+49 \cdot 64°$ in methyl alcohol solution.

The rotatory power of the preceding malic acid derivatives is less dependent on the size of the groups introduced than on their nature and position in the molecule. E. W. W.

Constitution of Camphoric Acid, and the Migrations which take place in its Molecule. By G. Blanc (*Compt. rend.*, 1900, **131**, 803—806. Compare Abstr., 1899, i, 300, 536; 1900, i, 507; Trans., 1900, **77**, 374, 1053).—The results obtained by the oxidation of inactive campholytic acid, prepared from *iso*lauronolic acid, were found to be in agreement with those obtained by Tiemann from active campholytic acid (this vol., i, 5). A lactone (campholytolactone of Tiemann) melting at 114—115° was obtained, and, on oxidation, the campholytic acid was converted into dimethyltricarballylic acid, melting at 156—157°. From these results, it follows that the constitution of campholytic acid is that which is given below. The conversion of campholytic acid into *iso*lauronolic acid is readily explained, if it is assumed that 1 mol. H_2O is first taken up, then a methyl group and a hydroxyl group change position, and that, finally, 1 mol. H_2O is eliminated, thus:



Campholytic acid.

*iso*Lauronolic acid.

The author concludes that Bouveault's formula for camphoric acid must be abandoned. H. R. Le S.

Compounds of Glycuronolactone. By G. Giemsa (*Ber.*, 1900, **33**, 2996—2998).—The *oxime* of glycuronolactone, $C_6H_9O_6N$, separates from alcohol in large, clear crystals, melts and decomposes at 149° and has $[\alpha]_D$ $+14·40°$; the normal *potassium* salt has $[\alpha]_D$ $+11·73°$.

The *semicarbazone*, $C_7H_{11}O_6N_3$, crystallises from hot water in long, white, silky needles, melts and decomposes at 188°, and has $[\alpha]_D$ $-20·83°$.

The *phenylbenzyhydrazone*, $C_{19}H_{20}O_5N_2$, crystallises from alcohol in long, white, silky needles, and melts, with decomposition, at 141°; the *potassium* salt crystallises in needles, melts at 176—178°, and has $[\alpha]_D$ $-20·29°$.

The *bromophenylhydrazone*, $C_{12}H_{13}O_5N_2Br$, crystallises from alcohol in square tablets, and melts, with decomposition, at 142°; the potassium salt is dextrorotatory.

The *phenylhydrazone*, $C_{12}H_{14}O_5N_2$, crystallises from alcohol in pale yellow needles, and melts at 160°. T. M. L.

Bromal Acetate, Acetylbromal Chloride and Bromide. By Emilio Gabutti (*Gazzetta*, 1900, **30**, ii, 191—196. Compare Abstr., 1900, i, 370).—*Bromal diacetate* (*βββ-tribromoethylidene diacetate*), $CBr_3·CH(OAc)_2$, obtained by the interaction of bromal and acetic anhydride, separates from ether in lozenge-shaped laminæ, which melt at 76°, and are soluble in alcohol; on prolonged boiling with concentrated aqueous sodium hydroxide, it yields bromoform and sodium acetate and formate.

Acetylbromal chloride (*α-chloro-βββ-tribromoethyl acetate*),

$$CBr_3·CHCl·OAc,$$

prepared by the action of acetyl chloride on bromal, is obtained as an oil boiling at 45° with partial decomposition; it is very soluble in alcohol or ether, and with hot concentrated alkali hydroxide solution yields bromoform and the acetate, formate, and chloride of the alkali metal.

Acetylbromal bromide (*αβββ-tetrabromoethyl acetate*),

$$CBr_3·CHBr·OAc,$$

is an oil boiling and decomposing at 75°; it is readily soluble in alcohol or ether, and with alkali hydroxides yields products similar to those obtained from the corresponding chloride. T. H. P.

Derivatives of α-Nitro-β-dinitropropaldehyde. By Joseph Torrey, jun., and Otis Fisher Black (*Amer. Chem. J.*, 1900, **24**, 452—465).—By the action of potassium nitrite on mucobromic acid, Hill and Sanger (Abstr., 1883, 47) obtained an orange-red salt, $C_3HO_7N_3K_2$. The authors find that this compound is the dipotassium salt of α-nitro-β-dinitropropionic acid; this view of its constitution was first suggested by the ease with which it is converted into the potassium salt of nitromalonaldehyde when heated with water or dilute alcohol (Hill and Torrey, Abstr., 1899, i, 788).

When this salt is treated with an ethereal solution of hydrogen chloride, *αββ-trinitropropaldehyde* is obtained on evaporation as a colourless oil which, if left for a few minutes at the ordinary temperature, undergoes violent decomposition. The *anil* crystallises in light yellow needles and decomposes at 90°; its *aniline, mono-* and *di-potassium,* and *barium* salts are described. The corresponding p-*tolil* and its p-*toluidine, mono-* and *di-potassium,* and *barium* salts were prepared. By the action of methylamine on the orange-red salt, the *monopotassium* salt of the methylimide of trinitropropionic acid is produced; when an aqueous solution of this salt is acidified with hydrochloric acid, the *methylimide* separates in white, pearly crystals; its *dipotassium* salt was also obtained. E. G.

Glyceraldehyde. By ALFRED WOHL and CARL NEUBERG (*Ber.*, 1900, **33**, 3095—3110. Compare Abstr., 1898, i, 555, and 1900, i, 11).—Details of the preparation of glyceraldehyde from acraldehyde acetal are given. The aldehyde forms colourless, pointed needles or prisms which frequently form stellate aggregates, and, like carbohydrates in general, it is sparingly soluble in organic media, but dissolves somewhat readily in water. It may be removed from aqueous solution by means of lead acetate and ammonia, but the resulting white pulverulent precipitate, when suspended in water and decomposed with hydrogen sulphide, yields a liquid which does not reduce Fehling's solution.

Glyceraldehydephenylmethylhydrazone, $OH\cdot CH_2\cdot CH(OH)\cdot CH:N_2MePh$, crystallises from a mixture of benzene and light petroleum in colourless, shining leaflets or prismatic needles which melt at 120°, but after solidification the substance does not fuse below 220°, when it decomposes with evolution of gas. The *diphenylhydrazone*, $C_3H_6O_2:N_2Ph_2$, resembles the foregoing compound, and melts at 133°. The p-*bromophenylosazone*, $OH\cdot CH_2\cdot C(N_2H\cdot C_6H_4Br)\cdot CH:N_2H\cdot C_6H_4Br$, melts at 168°.

Glyceraldehyde chlorohydrin (*α-chloro-β-hydroxypropaldehyde*),

$$OH\cdot CH_2\cdot CHCl\cdot CHO,$$

is prepared by the action of hypochlorous acid on acraldehyde acetal, the resulting acetate being hydrolysed by $N/10$ sulphuric acid; it distils with slight decomposition at 118° under a pressure of 30 mm. as a yellow, viscous liquid, and has an odour that is not unpleasant, although the vapour has a violent action on the mucous membrane. The p-*bromophenylhydrazone*, $C_3H_5OCl:N_2H\cdot C_6H_4Br$, separates from alcohol in slender, yellow needles melting at 61°.

When a dilute solution of glyceraldehyde and phloroglucinol is treated with a few drops of sulphuric acid, a gradual separation of colourless, pearly leaflets takes place, and is complete in about 10 hours. The new *substance*, $C_{15}H_{16}O_8$, is sparingly soluble in chloroform, benzene, ether, or hot water, but dissolves fairly readily in acetone, acetic acid, and ethyl acetate. When heated, it turns orange at 200°, and is not melted at 280°. The solution of the substance in sodium hydroxide reduces warm Fehling's solution, and also ammoniacal solutions of mercury and silver. The formation of this compound occurs in very dilute solutions, and is characteristic of glyceraldehyde.

Glyceraldoxime, $OH\cdot CH_2\cdot CH(OH)\cdot CH\dot{:}NOH$, is a colourless, viscid liquid which is miscible with water, alcohol, or pyridine, but insoluble in ether. It gives a white precipitate with ammoniacal lead acetate in aqueous solution; the lead compound, $C_3H_7O_6NPb_3$, when heated turns yellow, and at a temperature slightly above 100° deflagrates, depositing small beads of metallic lead.

On heating the oxime with an equal weight of potassium hydroxide until effervescence occurs, and treating the hot mass with cold 50 per cent. acetic acid, glycolaldehyde is produced, and may be isolated in the form of its osazone, or one of the following new derivatives. *Glycolaldehyde diphenylosazone*, $C_2H_2(N\cdot NPh_2)_2$, forms light yellow needles melting at 207°, dissolves in warm acetic acid, producing an emerald-green solution, and imparts a dark violet coloration to sulphuric acid. *Glycolaldehyde* p-*nitrophenylosazone*, $C_2H_2(N\cdot NH\cdot C_6H_4\cdot NO_2)_2$, crystallises from a mixture of pyridine and toluene in claret-coloured, glistening needles, and from hot benzonitrile in scarlet, stellate aggregates of needles, and melts at 311°; it is nearly insoluble in the ordinary media, but dissolves readily in various nitrogenous organic liquids, including nitrobenzene, aniline, pyridine, and nitriles.

Under the influence of 1 per cent. aqueous potash at 0°, glyceraldehyde condenses to a hexose, which was identified as β-acrose.

A. L.

Solidification of Acetone. By CARLO FORMENTI (*L'Orosi*, 1900, **23**, 223—224).—On placing acetone in a test-tube surrounded by liquid air it almost immediately begins to diminish in volume, and then becomes transformed into a snow-white mass of minute crystals which quickly liquefy when removed from the liquid air. No intermediate syrupy condition, such as occurs with alcohol, was observed in either change.

T. H. P.

Platinum-Carbon Compounds. By WILHELM PRANDTL and KARL A. HOFMANN (*Ber.*, 1900, **33**, 2981—2983).—A compound, $PtCl_2,C_6H_{10}O$, identical with the product obtained by Zeise (*J. pr. Chem.*, 1837, **20**, 193) from platinic chloride and acetone, is formed by the action of mesityl oxide on a solution of chloroplatinic acid. When chloroform is boiled with chloroplatinic acid for several days, a product, $PtCl_2,C_2H_4$, may be obtained, crystallising from toluene in pale yellow needles which begin to decompose at 140°.

J. J. S.

Methyl Nonyl Ketone. By HENRI CARETTE (*J. Pharm.*, 1900, [vi], **12**, 217—222. Compare Abstr., 1899, i, 860).—Benzaldehyde and methyl nonyl ketone react in presence of a 0·25 per cent. alcoholic solution of potassium hydroxide to yield a compound, $C_{18}H_{26}O$; this forms nacreous crystals, melts at 41—42°, boils at 245° under 35 mm., but decomposes at 200° under atmospheric pressure, and is very readily soluble in boiling alcohol, ether, glacial acetic acid, or benzene.

With a 1 per cent. solution of potassium hydroxide in 95 per cent. alcohol in the cold this compound is formed, together with a polymeride, $C_{36}H_{52}O_2$, melting at 116°. If, however, the mixture is boiled immediately after the addition of the potassium hydroxide, the compound melting at 116° is the sole product. This compound crystallises in aggregates of slender needles, which are soluble in alcohol, ether, glacial acetic acid, or benzene; it decomposes at 200° under atmospheric pressure, but boils and decomposes at 310° under 35 mm. It is also obtained when the compound melting at 41—42° is boiled with a 1 per cent. solution of potassium hydroxide in 95 per cent. alcohol. H. R. Le S.

Acetylœnanthylidene and Benzoylœnanthylidene [Acetyl and Benzoylheptinene] and their Conversion by Hydration into β-Diketones. By Charles Moureu and Raymond Delange (*Compt. rend.*, 1900, **131**, 710—712. Compare Abstr., 1900, i, 20, 397).—*a-Acetylheptinene*, $CH_2Me{\cdot}[CH_2]_3{\cdot}C\vdots CAc$, produced by adding acetic chloride to the sodium derivative of heptinene suspended in ether, is a liquid with a pungent odour; it boils at 91—93° under 18 mm. pressure, has a sp. gr. 0·8819 at 0° and n_D 1·4453 at 24°.

Acetylhexoylmethane, $CH_2Me{\cdot}[CH_2]_4{\cdot}CO{\cdot}CH_2Ac$, obtained by hydrating the preceding compound through the agency of sulphuric acid, is a colourless liquid boiling at 105—107° under 22 mm. pressure, and has a sp. gr. 0·9378 at 0°; it solidifies at $-23°$ and melts at $-18°$.

a-Benzoylheptinene, $CH_2Me{\cdot}[CH_2]_3{\cdot}C\vdots CBz$, prepared in a similar manner to the corresponding acetyl derivative, boils at 177—179° under 19 mm. pressure, solidifies at $-23°$ and melts at $-5°$.

Benzoylhexoylmethane, $CH_2Me{\cdot}[CH_2]_3{\cdot}CO{\cdot}CH_2Bz$, formed by the action of sulphuric acid on the preceding substance, boils at 185—186° under 18 mm. pressure.

These diketones give the reactions characteristic of β-diketones; they yield blue copper salts soluble in chloroform, develop red colorations with alcoholic solutions of ferric chloride, and are decomposed by alkalis. G. T. M.

Decomposition of Ketones of Acetylenic Function by means of Alkalis. By Charles Moureu and Raymond Delange (*Compt. rend.*, 1900, **131**, 800—803. Compare Abstr., 1900, i, 397).—An aqueous solution of potassium hydroxide has no action on a-acetylheptylinene or a-benzoylheptylinene in the cold, but when boiling, it hydrolyses the former into meythyl amyl ketone, acetone, hexoic acid, and acetic acid, and the latter into methyl amyl ketone, acetophenone, hexoic acid, and benzoic acid. These two decompositions are easily explained if it is assumed that, before hydrolysis takes place, a diketone is formed by the addition of a mol. of water.

H. R. Le S.

Disulphones. IV. Mercaptoles and Sulphones from Diketones. By Theodor Posner (*Ber.*, 1900, **33**, 2983—2993. Compare Abstr., 1899, i, 604; 1900, i, 5, 16).—a-, β-, or γ-Diketones which contain both carbonyl groups attached to methyl radicles, for example, diacetyl, acetylacetone, acetonylacetone, readily react with 4 mols. of a mercaptan, yielding dimercaptoles, and these on oxidation yield tetrasulphones.

If, however, one of the carbonyl groups in an α- or β-diketone is attached to a substituted methyl group, as in acetylpropionyl, methylacetylacetone, or benzoylacetone, the ketone reacts with only 2 mols. of a mercaptan, yielding a ketomercaptole, which on oxidation gives a ketodisulphone. In the case of benzil, the condensation only occurs in the presence of zinc chloride, and then the product is a ketomercaptole, which on oxidation is converted back into its constituents. γ-Diketones always yield dimercaptoles, and these on oxidation form tetrasulphones.

Similar reactions are met with in substituted ethyl acetoacetates.

ββγγ-Tetraethylthiolbutane (*diacetyldimercaptole*),

$$\mathrm{CMe(SEt)_2{\cdot}CMe(SEt)_2},$$

on oxidation with cold saturated potassium permanganate, yields the corresponding *tetrasulphone*, $\mathrm{C_2Me_2(SO_2Et)_4}$, which crystallises from alcohol in large prisms melting at 76—81° (corr.). *ββ-Diethylsulphonepentane-γ-one* (*acetylpropionyldisulphone*), $\mathrm{CMe(SO_2Et)_2{\cdot}COEt}$, crystallises in rhombic plates melting at 48—49°. *Acetyl*iso*butyryldisulphone* (*ββ-diethylsulphone-δ-methylpentane-γ-one*), crystallises in colourless plates melting at 81—82°.

αβ-Diphenyl-α-diethylthiolethane-β-one (*benzilmercaptole*),

$$\mathrm{CPh(SEt)_2{\cdot}COPh},$$

forms monoclinic crystals melting at 59·5—60°. By the condensation of benzoin with ethyl mercaptan in the presence of hydrogen and zinc chlorides, a substance, $\mathrm{C_{18}H_{20}S_2}$, the constitution of which has not been determined, is obtained.

ββγγ-Tetraethylthiolpentane (*acetylacetonetetrasulphone*),

$$\mathrm{CH_2[CMe(SO_2Et)_2]_2},$$

forms thick, rounded crystals melting at 111°. *β-Diethylsulphone-γ-methylpentane-δ-one* (*methylacetylacetoneketodisulphone*),

$$\mathrm{CMe(SO_2Et)_2{\cdot}CHMeAc},$$

crystallises in colourless plates melting at 122—123°.

α-Phenyl-γ-diethylsulphonbutane-α-one (*benzoylacetoneketodisulphone*), $\mathrm{COPh{\cdot}CH_2{\cdot}CMe(SO_2Et)_2}$, crytallises in colourless plates melting at 109—111°.

ββεε-Tetraethylsulphonehexane, $\mathrm{C_2H_4[CMe(SO_2Et)_2]_2}$, crystallises from acetic acid in iridescent plates melting at 200—201°. *β-Methyl-γγζζ-tetraethylsulphoneheptane* (*dimethylacetonylacetonetetrasulphone*),

$$\mathrm{CHMe_2{\cdot}C(SO_2Et)_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe(SO_2Et)_2},$$

forms a crystalline powder melting at 129—131°.

The ketodisulphone derivatives which contain a free carbonyl group do not react with hydroxylamine, phenylhydrazine, or semicarbazide.

J. J. S.

Carbohydrates of Carageen Moss. By J. Šebor (*Chem. Centr.*, 1900, ii, 846—847; from *Oesterr. Chem.-Zeit.*, 3, 441—444).—The alga *Chondrus crispus*, from which the mucilage was prepared, on oxidation yielded 23·4 per cent. of mucic acid corresponding with 29·6 of galactose and when distilled with a 12 per cent. solution of hydrochloric acid gave 1·2 per cent. of furfuraldehyde corresponding with 2·5 of pentosans. By extracting the moss with water and precipitating with alcohol, the mucilage is obtained as an amorphous, yellowish-brown powder, which swells when immersed in water, and becomes brown when treated with iodine. The cells of the algæ also contain proteids and salts. The dry jelly free from ash yields 41·9 per cent. of galactose (= 37·8 of galactan) and 4·1 of pentoses (= 3·6 of pentosans). In the product obtained by treating the algæ with a 0·5 per cent. solution of sulphuric acid, galactose, dextrose, and lævulose were detected but neither arabinose nor xylose. The mucilage appears to be a complex carbohydrate formed from galactose, dextrose, and lævulose or a mixture of galactan with glucosan and lævulosan, and a small quantity of a pentosan which is probably xylan; the sugars are not present, however, in the proportions contained in raffinose. The carbohydrate has probably a large molecular weight and like starch serves as a store of nutriment for the plant. E. W. W.

Cellulose, Hydrocelluose, Mercerised and Precipitated Cellulose. By Léo Vignon (*Compt. rend.*, 1900, **131**, 708—709. Compare Bumcke and Wolffenstein, Abstr., 1899, i, 852).—The properties of cotton cellulose, hydrocellulose, mercerised and precipitated cellulose differ markedly from those of oxycellulose; for example, the former substances have no reducing action on solutions of copper salts and furnish far smaller quantities of sugar when heated for six hours with dilute hydrochloric acid, cellulose and its derivatives yielding from 3·3 to 4·4 per cent. of reducing sugar, whereas oxycellulose gives rise to 14·7 per cent. of this product.

The heats of combustion of cellulose, hydrocellulose, mercerised cellulose and precipitated cellulose are 4223, 4006, 3980, and 3982 cal. respectively. The concentrated solutions of alkalis employed in mercerising cotton and the dilute acids used in forming Girard's hydrocellulose, hydrate and probably depolymerise cellulose without conferring on the substance any new chemical properties. Oxycellulose, on the other hand, cannot exist in concentrated alkaline solutions as it breaks up into cellulose and a soluble acid, behaving under these conditions like furfuraldehyde which yields furfurylic alcohol and pyromucic acid. G. T. M.

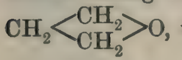
Amino-alcohols. By Louis Henry (*Chem. Centr.*, 1900, ii, 1008—1009; from *Bull. Acad. roy. Belg.*, **38**, 584—606).—*γ-Aminobutyl alcohol*, $NH_2·CH_2·CH_2·CH_2·CH_2·OH$, prepared by the action of sodium on an alcoholic solution of β-cyanopropyl alcohol, is a colourless liquid, boils at 125° and 206° under pressures of 34 and 776 mm. respectively, is soluble in alcohol but insoluble in ether, has a sp. gr. 0·967 at 12°, and dissolves in water with development of heat, forming a hydrate. The *dibenzoyl* derivative, $NHBz·C_4H_8·OBz$, crystallises in needles and melts at 58°. By the action of nitrous acid on aminobutyl alcohol, tetramethylene glycol and butylene glycol,

$$OH·CH_2·CH_2·CHMe·OH,$$

are formed, and by the action of formaldehyde, the compound $OH·CH_2·NH·C_4H_8·OH$ is obtained.

Aminoisopropyl alcohol, $NH_2·CH_2·CHMe·OH$, prepared by reducing the corresponding nitro-compound with iron and acetic acid, boils at 160° under 750 mm. pressure.

When groups, such as OH, Cl, NO_2, are replaced by the amino-group in compounds containing two or three carbon atoms, the boiling point of the product is always high when an amino-alcohol, $X\cdot CH(OH)\cdot CH_2\cdot NH_2$, is formed. This is explained by assuming a reaction to occur between the OH and the NH_2 group, a theory which derives support from the fact that heat is developed when liquid amines, such as diethylamine, *iso*butylamine, *iso*amylamine, or piperidine, are dissolved in methyl or ethyl alcohol, whilst their solution in ethyl acetate or ether is not attended by any development of heat. The amino-alcohols of the types $OH\cdot CH_2\cdot NR_2$ or $OH\cdot C\cdot C\cdot NH_2$ combine with hydrogen cyanide, amines, or aliphatic nitro-compounds, with elimination of water, to form compounds such as $CN\cdot CH_2\cdot NMe_2$, $NMe_2\cdot CH_2\cdot NMe_2$, or $NO_2\cdot C(CH_2\cdot C_5NH_{10})_3$, but aminobutyl alcohol does not give these reactions.

Since the oxide, $CH_2<\begin{matrix}CHMe\\CHMe\end{matrix}>O$, unlike ethylene oxide, is incapable of acting on ammonia or amines, probably trimethylene oxide,  $CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}>O$, would behave in this respect like the former.

E. W. W.

2 : 1-Aminopropanol and 2 : 3-Aminobutanol. By Eduard Strauss (*Ber.*, 1900, **33**, 2825—2830).—2 : 1-*Aminopropanol* (amino-*iso*propyl alcohol), $NH_2\cdot CH_2\cdot CHMe\cdot OH$, is produced when an aqueous solution of *iso*nitrosoacetone is treated with successive small quantities of sodium amalgam and hydrochloric acid, and is isolated by evaporating to dryness, and distilling the residue with potassium hydroxide. It boils at 156—158° under atmospheric pressure, and when heated at 100° with fuming hydrobromic acid yields β-bromopropylamine. The *platinichloride*, $(C_3H_9ON)_2,H_2PtCl_6$, crystallises in yellow leaflets melting at 200°. *β-Hydroxypropylphenylthiocarbamide*,

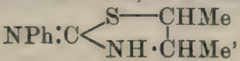
$C_3H_7O\cdot NH\cdot CS\cdot NHPh$,

forms needles melting at 106·5°.

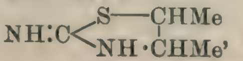
2 : 3-*Aminobutanol* (γ-amino-*sec*.butyl alcohol),

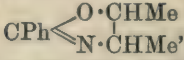
$NH_2\cdot CHMe\cdot CHMe\cdot OH$,

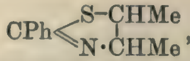
from *iso*nitrosomethyl ethyl ketone, boils at 155—158° under atmospheric pressure. The *platinichloride*, $(C_4H_{11}ON)_2,H_2PtCl_6$, forms orange leaflets which melt at 185°.

Phenyl-β-hydroxybutylthiocarbamide, $C_4H_9O\cdot NH\cdot CS\cdot NHPh$, crystallises in hard, white needles melting at 76—78°. When heated with strong hydrobromic acid, it is converted into N-*phenylbutylene-ψ-thiocarbamide*,  $NPh{:}C<\begin{array}{l}S—CHMe\\NH\cdot \overset{|}{C}HMe\end{array}$, which crystallises in needles melting at 114° and gives a *picrate*, $C_{11}H_{14}N_2S,C_6H_3O_7N_3$, melting at 186°.

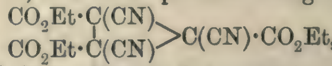
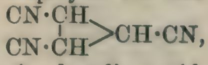
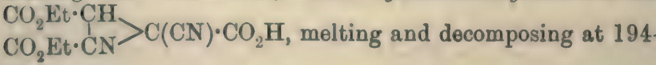
βγ-Bromoaminobutane, $CHMeBr\cdot CHMe\cdot NH_2$, was isolated in the form of its *picrate*, $C_4H_{10}NBr,C_6H_3O_7N_3$, which crystallises from water in yellow needles melting at 165—166°.

Butylene-ψ thiocarbamide,  $NH{:}C<\begin{array}{l}S—CHMe\\NH\cdot \overset{|}{C}HMe\end{array}$, is a brownish oil, and gives a *picrate*, $C_5H_{10}N_2S,C_6H_3O_7N_3$, crystallising in prisms and melting at 199—200°, and a *platinichloride*, $(C_5H_{10}N_2S)_2,H_2PtCl_6$, crytallising in tablets and melting at 188—195°.

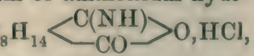
2-*Phenyl*-4 : 5-*dimethyloxazoline*, 
$\mathrm{CPh}\!<\!\begin{array}{l}\mathrm{O\cdot CHMe}\\ \quad|\\ \mathrm{N\cdot CHMe}\end{array}$, was obtained as a yellowish oil. The *platinichloride*, $(C_{11}H_{13}ON)_2,H_2PtCl_6$, forms leaflets melting at 193·5°, and the *picrate*, $C_{11}H_{13}ON,C_6H_3O_7N_3$, needles melting at 133°.

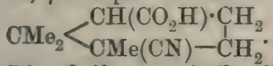
2-*Phenyl*-4 : 5-*dimethylthiazoline*, 
$\mathrm{CPh}\!<\!\begin{array}{l}\mathrm{S{-}CHMe}\\ \quad|\\ \mathrm{N\cdot CHMe}\end{array}$, forms a yellow oil. The *platinichloride*, $(C_{11}H_{13}NS)_2,H_2PtCl_6$, crystallises in bright red needles melting and decomposing at 179—180°, and the *picrate*, $C_{11}H_{13}NS,C_6H_3O_7N_3$, in yellow leaflets melting at 164—165°.

2-*Mercapto*-4 : 5-*dimethylthiazoline* separates from water in beautiful needles melting at 53—58°. A. L.

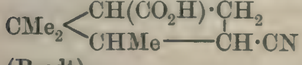
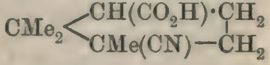
Action of Halogens on Ethyl Sodiocyanoacetate. By GIORGIO ERRERA and F. PERCIABOSCO (*Ber.*, 1900, 33, 2976—2981. Compare Thorpe and Young, Trans., 1900, 77, 936).—The reaction between iodine or bromine and ethyl sodiocyanoacetate proceeds best in ethereal solution, the chief product being *ethyl tricyanotrimethylenetricarboxylate*, 
$\begin{array}{l}\mathrm{CO_2Et\cdot C(CN)}\\ \qquad\quad|\\ \mathrm{CO_2Et\cdot C(CN)}\end{array}\!>\!\mathrm{C(CN)\cdot CO_2Et}$, which crystallises from dilute alcohol in needles or flat crystals melting at 119°; it is probably identical with the substance described by Thorpe and Young as ethyl dicyanosuccinate, which melts at 120°. Various other products have been isolated, but have not yet been investigated. Alkalis readily hydrolyse the ester; when barium hydroxide is employed, the product is trimethylenetetracarboxylic acid, melting at 193—194° (Abstr., 1885, 1125, and 1895, i, 269); when heated at 200°, this acid yields trimethylenetricarboxylic acid, melting at 215°. When cold dilute barium hydroxide solution is employed for the hydrolysis, the products are *tricyanotrimethylene*, 
$\begin{array}{l}\mathrm{CN\cdot CH}\\ \qquad|\\ \mathrm{CN\cdot CH}\end{array}\!>\!\mathrm{CH\cdot CN}$, melting at 182—184°, and *cyanotrimethylenetricarboxylic acid*, 
$\begin{array}{l}\mathrm{CO_2Et\cdot CH}\\ \qquad\quad|\\ \mathrm{CO_2Et\cdot CN}\end{array}\!>\!\mathrm{C(CN)\cdot CO_2H}$, melting and decomposing at 194—195°.

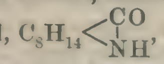
J. J. S.

Peculiar Disruption of the Camphor Ring. By FERDINAND TIEMANN (*Ber.*, 1900, 33, 2953—2959).—[With GEORG LEMME and MAX KERSCHBAUM].—By the action of potassium or ammonium hydroxide on α-camphor*iso*imide hydrochloride, 
$C_8H_{14}\!<\!\begin{array}{c}\mathrm{C(NH)}\\ \mathrm{CO}\end{array}\!>\!O,HCl$, Hoogewerff and van Dorp obtained cyanolauronic acid (Abstr., 1896, i, 314), which melts at 151—152°; the authors have prepared this compound by the action of acetic anhydride on *iso*nitrosocamphor, and call it *α-camphornitrilic acid.* *β*-Camphor*iso*imide hydrochloride yields the corresponding cyano-acid, which Hoogewerff and van Dorp called cyanodihydrocampholytic acid (*loc. cit.*), and the authors, *β-camphor-*

nitrilic acid. Expecting that distillation of the calcium salts would convert these substances into the nitriles of α-campholytic and lauronolic acids respectively, the present investigators have discovered that a more profound change takes place, both compounds yielding αε-dimethylheptenonitrile, which is oxidised by potassium permanganate to acetone, methylglutaric acid, $CO_2H\cdot CH_2\cdot CH_2\cdot CHMe\cdot CO_2H$, and methylsuccinic acid, $CO_2H\cdot CH_2\cdot CHMe\cdot CO_2H$. A disruption of the camphor ring has thus taken place between the methylated and the dimethylated carbon atoms, and the production of the same nitrile from both acids can be explained only, in the authors' opinion, by the migration of a cyano-group. According to Bredt's camphor formula, β-camphornitrilic acid would be represented by the expression  $\mathrm{CMe_2}{<}\begin{matrix}\mathrm{CH(CO_2H)\cdot CH_2}\\ \mathrm{CMe(CN)-CH_2}\end{matrix}$.

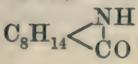
αε-Dimethylheptenonitrile, $CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CHMe\cdot CN$, boils at 92—95° under 16 mm. pressure, has a sp. gr. 0·8563 at 17°, and n_D 1·4486. *αε-Dimethylheptenoic acid,* $CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CHMe\cdot CO_2H$, boils at 140—141° and 236—240° under pressures of 18 mm. and 760 mm. respectively, has a sp. gr. 0·934 at 17°, and n_D 1·4501; the *amide* crystallises from benzene and melts at 84°. M. O. F.

Constitution of β-Camphornitrilic Acid. By FERDINAND TIEMANN (*Ber.*, 1900, **33**, 2960—2965).—[With HERMANN TIGGES.]—In the case of α-camphornitrilic acid it can be shown that it is the nitrile corresponding with α-camphoramic acid by partial hydrolysis to this substance, but β-camphornitrilic acid does not undergo this change. In order to prove that it corresponds with β-camphoramic acid, it has been converted into the amide, $(\beta)CN\cdot C_8H_{14}\cdot CO\cdot NH_2(\alpha)$, which was then oxidised with sodium hypobromite to the nitrile of amino[dihydro]lauronolic acid, $CN\cdot C_8H_{14}\cdot NH_2$, this being hydrolysed to the acid. If it is admitted that the carboxyl group of amino[dihydro]lauronolic acid occupies the position of the carbonyl group of camphor, the cyano-group of β-camphornitrilic acid also must be in the β-position, and the transformation of β-camphoramic acid into β-camphornitrilic acid is therefore normal, and is not attended by molecular rearrangement; the constitution of the last-named substance will be represented by one of the formulæ,  $\mathrm{CMe_2}{<}\begin{matrix}\mathrm{CH(CO_2H)\cdot CH_2}\\ \mathrm{CHMe-\!\!-CH\cdot CN}\end{matrix}$ (Tiemann), and  $\mathrm{CMe_2}{<}\begin{matrix}\mathrm{CH(CO_2H)\cdot CH_2}\\ \mathrm{CMe(CN)-CH_2}\end{matrix}$ (Bredt).

The *amide* of β-camphornitrilic acid, $(\alpha)CN\cdot C_8H_{14}\cdot CO\cdot NH_2(\beta)$, crystallises from water or alcohol in white prisms, and melts at 194—196°. When treated with bromine and sodium hydroxide, it yields the *compound*, $C_{19}H_{32}ON_4$, melting at 293°, and the *acid*, $C_{10}H_{18}O_3N_2$, which melts and decomposes at 173°, dissolves readily in dilute mineral acids, yields *iso*lauronolic acid under the influence of concentrated acids, and is resolved on dry distillation into carbon dioxide, ammonia, and the anhydride of aminodihydrocampholytic acid,  $\mathrm{C_8H_{14}}{<}\begin{matrix}\mathrm{CO}\\ \mathrm{NH}\end{matrix}$, which melts at 189°. The *nitrile* of amino[dihydro]lauronolic acid is another product of oxidising the amide of β-camphornitrilic acid with alkali hypobromite; the *hydro-*

chloride and *picrate* melt at 290° and 232° respectively, and hydrolysis in sealed tubes at 200° converts it into amino[dihydro]lauronolic acid. The *base*, $C_{17}H_{27}N_3$, is produced along with the nitrile of amino[dihydro]-lauronolic acid; it crystallises from petroleum, melts at 132—133°, and forms a sparingly soluble aurichloride and platinichloride.

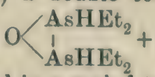
The *amide* of α-camphornitrilic acid melts at 130—131°, and yields with alkali the *base*, $C_{10}H_{16}ON_2$, which melts at 280°. The *acid*, $C_{10}H_{18}O_3N_2$, obtained by the action of alkaline hypobromite, crystallises from ethyl acetate in long needles containing $\frac{1}{2}H_2O$; it melts first at 105°, liberating water, then solidifies, and finally decomposes and fuses at 199—200°, yielding the anhydride of amino[dihydro]lauronolic acid,



$C_8H_{14}<\begin{matrix}NH\\ |\\ CO\end{matrix}$, which melts at 201°. M. O. F.

Action of Alkaline Sulphides on Potassium Ferrocyanide. By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1900, 21, [vii], 204).—No thermal change is observed on mixing dilute solutions of potassium ferrocyanide and sodium sulphide, but nevertheless a slow chemical reaction takes place, resulting in the formation of ferrous sulphide. The ferrocyanide in dilute solutions is slightly dissociated into simple cyanides, and the ferrous cyanide which results, interacts with sodium sulphide yielding ferrous sulphide and sodium cyanide; the presence of the latter cyanide, however, diminishes the dissociation of the double cyanide, and hence a state of equilibrium is soon attained and the amount of sulphide precipitated is very small. G. T. M.

Arsenical Gas from Wall-paper. By PIETRO BIGINELLI (*Atti Real. Accad. Lincei*, 1900, [v], 9, ii, 210—214 and 242—249).—On growing pure cultures of the arsenic mould, *Penicillium brevicaule*, obtained by Gosio (*Riv. d'ig. e san. pubbl.*, 1892, 223) in presence of sodium arsenite, energetic decomposition takes place with evolution of gas which, when passed into a hydrochloric acid solution of mercuric chloride, causes the separation of colourless, tabular, triclinic crystals of the double *compound* $AsHEt_2 + 2HgCl_2$, or $AsHEt_2\colon AsHEt_2 + 4HgCl_2$, [$a : b : c = 1{\cdot}54787 : 1 : 2{\cdot}37709$; $\alpha = 126°8'30''$; $\beta = 123°14'$; $\gamma = 85°41'30''$]. When heated, it begins to soften at 239—240° and decomposes at 255—256°. It can be sublimed in a current of dry air at 100—110°, whilst, on standing in the air, it evolves an odour of garlic, and becomes slightly darkened. When treated with boiling water it dissolves, and on cooling the liquid, it deposits (1) a small quantity of a *compound* separating in minute prismatic crystals and melting and decomposing at 250—251°. (2) a double *compound* of tetraethyldiarsonium with mercuric chloride,



$O<\begin{matrix}AsHEt_2\\ |\\ AsHEt_2\end{matrix} + 4HgCl_2$, crystallising in shining scales which, when heated in a sealed tube, undergo contraction and incipient fusion at about 270°, but do not melt or completely decompose even at 290°. When the latter compound is treated, in presence of a small quantity of water and an excess of ether, with solid alkali hydroxide, and afterwards with an ethereal solution of iodine, *tetraethyldiarsonium iodide*, $O(AsHEt_2I)_2$, is obtained in slender, straw-coloured, hygroscopic needles melting at 102°, and this, with silver sulphate, yields the corresponding *sulphate*, $C_8H_{22}OAs_2(SO_4)$, melting at 210°. With silver oxide, the iodide yields *tetraethyldiarsonium oxide*(?), $AsHEt_2{<}{}^{O}_{O}{>}AsHEt_2$, in the form of tufts of deliquescent needles, whilst with nitric acid and potassium permanganate it gives a double *compound* of tetraethyldicacodylic acid and potassium nitrate, $O(AsHEt_2{\cdot}OH)_2,KNO_3$, separating from alcohol in hygroscopic, acicular, prismatic crystals which melt at 129—131° and explode at higher temperatures.

If the gas evolved by the *Penicillium brevicaule* is passed into mercuric nitrate solution an infusible, insoluble, yellow, amorphous *powder* of the composition $AsHEt_2,2HgNO_3$ is deposited.

It is concluded that the gas developed by wall-paper containing arsenic, and to which poisoning is due, is diethylarsine. T. H. P.

Action of Concentrated Nitric Acid on Bromobenzene. By Ernst Bandrowski (*Chem. Centr.*, 1900, ii, 848; from *Bull. Acad. Sci. Cracow*, 1900, 193—198).—By the action of nitric acid of sp. gr. 1·5 on bromobenzene, 1 : 2 : 4-bromodinitrobenzene is always formed, together with *o*- and *p*-bromonitrobenzene (compare Parry, Abstr., 1896, i, 352). By the action of *p*-phenylenediamine on the crude product, a red, crystalline substance is obtained, whereas pure bromonitrobenzene does not react with phenylenediamine. When this red substance is boiled with dilute hydrochloric acid, Nietzki and Ernst's dinitrophenylaminodiphenylamine (Abstr., 1890, i, 1114) goes into solution, whilst *tetranitrodiphenyl*-p-*phenylenediamine*,

$$C_6H_4[NH{\cdot}C_6H_3(NO_2)_2]_2,$$

remains undissolved. Both these compounds have been found to be formed by the action of phenylenediamine on pure 1 : 2 : 4-bromodinitrobenzene. The tetranitro-derivative separates from nitrobenzene in dark red crystals, has a high melting point, and is insoluble in most solvents and in acids. *o*-Bromonitrobenzene is isolated either by distilling in steam or by removing the bromodinitrobenzene in the form of the insoluble dinitrophenylbenzidine by heating the crude product with benzidine and alcohol on the water-bath; under these conditions, *o*-bromonitrobenzene does not act on benzidine, hence Schöpf's *o*-bromonitrobenzene (Abstr., 1889, i, 772) must have been impure, and his product was doubtless dinitrophenylbenzidine.

E. W. W.

m-Nitrobenzyl Derivatives. By Attilio Purgotti and C. Monti (*Gazzetta*, 1900, 30, ii, 246—260).—m-*Nitrobenzyl-ω-sulphonic acid*, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}SO_3H$, obtained as its sodium salt by the action of sodium sulphite on *m*-nitrobenzyl chloride, separates from water with $1H_2O$ in the form of minute, white crystals melting at 74°; it is very soluble in alcohol and decomposes alkali carbonates. The *sodium* (with H_2O), *barium* (with $3H_2O$), *lead*, and *silver* salts were prepared; the *methyl* ester forms small crystals melting at 77°, and soluble in ether or alcohol.

m-*Nitrobenzyl-ω-sulphonic chloride* separates from benzene in colourless, rhombic crystals [$a : b : c = 1{\cdot}86569 : 1 : 0{\cdot}90405$] with a vitreous lustre melting at 100°.

m-*Nitrobenzyl-ω-sulphonamide*, crystallises from water in thin, sparkling laminæ which melt and decompose at 159°, and are moderately soluble in alcohol, more so in hot water.

m-*Aminobenzyl-ω-sulphonic acid*, obtained by reducing the nitro-acid in alcoholic solution with ammonium sulphide, separates on the addition of alcohol to its aqueous solution as a white, crystalline precipitate which does not melt, but decomposes at a high temperature.

m-*Nitrobenzylaniline*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NHPh$, prepared by the action of aniline on *m*-nitrobenzyl chloride in alcoholic solution, crystallises from alcohol in slender, orange-red, sparkling needles which melt at 84·5° and are moderately soluble in ether, and more so in alcohol, benzene, chloroform, or carbon disulphide. With acids, it forms readily dissociable salts, its *hydrochloride* forming white leaves or scales which are decomposed by water. *Acetyl*-m-*nitrobenzylaniline*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NPhAc$, crystallises from ether in long, yellow needles melting at 48° and soluble in chloroform, alcohol, or benzene.

m-*Aminobenzylaniline*, $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot NHPh$, forms long, slender needles which melt at 60°, and are soluble in all the ordinary solvents; its *hydrochloride* melts at 161°.

m-*Nitrobenzyl*-o-*toluidine*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot C_6H_4Me$, prepared similarly to the aniline derivative, crystallises from alcohol in sparkling, orange-yellow scales melting at 62°, and dissolves in benzene, chloroform, carbon disulphide, or ether; the *hydrochloride* separates from hydrochloric acid solutions in white, sparkling leaflets which begin to decompose at 100° and are also decomposed by water, even in the cold.

m-*Nitrobenzyl*-m-*toluidine*, crystallises from alcohol in microscopic tufts of elongated laminæ which melt at 67° and are soluble in benzene, chloroform, carbon disulphide, or ether, whilst its *hydrochloride* separates from hydrochloric acid in shining white needles which are decomposed by cold water or by heating above 100°.

m-*Dinitrodibenzyl*-p-*toluidine*, $C_6H_4Me \cdot N(CH_2 \cdot C_6H_4 \cdot NO_2)_2$, crystallises from alcohol in slender, lustrous, yellow needles melting at 86° and is soluble in benzene, chloroform, or carbon disulphide, and to a less extent in ether.

T. H. P.

Iodination of Alkylbenzenes. By Albert Edinger and Paul Goldberg (*Ber.*, 1900, **33**, 2875—2883).—Alkylbenzenes readily give a good yield of monoiodo-derivatives when warmed for several hours at 100° with light petroleum, powdered sulphur iodide, and an excess of dilute nitric acid of sp. gr. 1·34; in all cases, the iodine enters the nucleus exclusively. With benzene, 50 per cent. of the calculated quantity of iodobenzene is obtained, and with toluene 60—70 per cent. of a mixture of *o*- and *p*-iodotoluenes. *m*-Xylene yields 75 per cent. of *p*-iodo-*m*-xylene, which boils at 220° (Hammerich, Abstr., 1890, 1106, gives 231°) and gives iodotoluic acid [$Me : CO_2H : I = 1 : 3 : 6$] when oxidised with a mixture of potassium permanganate and dilute nitric acid; the corresponding iodo*iso*phthalic acid could not be obtained, since, on using more concentrated nitric acid in the oxidation, a *diiodoisophthalic* acid is formed, which crystallises from dilute acetic acid, melts and decomposes at 190° and yields a *copper* salt with $2H_2O$. p-*Iodo*-o-*xylene* boils at 225°, and on oxidation with a mixture of potassium permanganate and dilute nitric acid, yields a *diiodophthalic acid*, melting and decomposing at 195°; with dilute nitric acid alone, a mixture of this acid with 4-iodophthalic acid is obtained. *Iodo-p-xylene* boiling at 217°, iodomesitylene (Töhl, Abstr., 1892, 967), and iododurene were obtained from the corresponding hydrocarbons in yields of from 70—80 per cent. of the theoretical; *iodopentamethylbenzene* crystallises from alcohol in white, lustrous plates and melts at 127°, whilst *iodocymene* boils at 80° under 5 mm. pressure. In the case of cymene, the yield of iodo-derivative is only 30—35 per cent. of that calculated, owing to oxidation occurring, whilst from naphthalene a mixture of α- and β-iodonaphthalenes (the latter in very small amount) with nitronaphthalene is obtained, which can only be purified with difficulty. W. A. D.

Bromination of Alkylbenzenes. By Albert Edinger and Paul Goldberg (*Ber.*, 1900, **33**, 2883—2885).—Although sulphur chloride cannot be profitably used to chlorinate alkylbenzenes, sulphur bromide gives good results in brominating; the method adopted is the same as in iodination (preceding abstract), with the exception that the mixture is well cooled during the action. Benzene, toluene, *o*-, *m*-, and *p*-xylene, mesitylene, pentamethylbenzene, and naphthalene give rise only to monobromo-derivatives, but durene yields dibromodurene.

W. A. D.

Application of the Reducing Action of Hyposulphurous Acid. By Paul Goldberger (*Chem. Centr.*, 1900, ii, 1014; from *Oesterr. Chem.-Zeit.*, **3**, 470).—Nitro-compounds containing acid or basic groups are easily reduced by adding zinc dust to a solution of sodium hydrogen sulphite containing the nitro-compound. Neutral compounds such as nitrobenzene or dinitrobenzene are not reduced by this means, but from *p*-nitrophenol, 80 per cent. of the calculated yield of *p*-aminophenol may be obtained; similarly, nitroaniline gives 77 of *p*-phenylenediamine and nitrobenzoic acid 90 per cent. of the calculated yield of anthranilic acid. E. W. W.

Substituted Nitrogen Chlorides and Bromides derived from *o*-, *m*-, and *p*-Nitroacetanilide. By Frederick D. Chattaway, Kennedy J. P. Orton, and Robert C. T. Evans (*Ber.*, 1900, **33**, 3057—3062. Compare Trans., 1898, **73**, 1047; 1899, **75**, 134, 789, 797, 800; Abstr., 1900, i, 152).—The presence of a nitro-group in acyl chloro- and bromo-amino-derivatives renders more difficult their change into the corresponding chloro- and bromo-substitution products. Derivatives of *m*- and *p*-nitroacetanilide change very slowly in acetic acid solution, a considerable amount of hydrolysis taking place at the same time, whilst derivatives of *o*-nitroacetanilide do not undergo the change in these circumstances, but yield the corresponding substituted anilines when they are heated under slightly acidified water.

Acetylchloroamino-o-nitrobenzene, $NO_2 \cdot C_6H_4 \cdot NClAc$, is prepared by the action of bleaching powder on *o*-nitroacetanilide in acetic acid solution, and crystallises in short prisms melting at 80°. It does not undergo change in acetic acid solution, but when heated with water containing a few drops of acid it yields *o*-nitro-*p*-chloroaniline, melting at 116°.

Acetylbromoamino-o-*nitrobenzene* crystallises in yellow prisms melting at 141°, and when heated with acidified water yields *o*-nitro-*p*-bromoaniline. *Acetylchloroamino*-m-*nitrobenzene* crystallises in faintly yellow prisms melting at 102°. When its solution in acetic acid is left for some time, *m*-nitroacetanilide and a mixture of *m*-nitro-*p*-chloroacetanilide, and 3-nitro-6-chloroacetanilide is formed, the *m*-nitro-*p*-chloro-compound being produced in the larger proportion. *Acetylbromoamino*-m-*nitrobenzene* forms lustrous, yellow prisms melting at 135—136°, and readily undergoes intramolecular change in acetic acid solution. The resulting anilides yield on hydrolysis *m*-nitro-*p*-bromoaniline as chief product. *Acetylchloroamino*-p-*nitrobenzene* crystallises in yellow prisms melting at 110—111°, and in acetic acid solution yields *p*-nitroacetanilide and *o*-chloro-*p*-nitroacetanilide, melting at 143°. When the nitrogen chloride is heated with sodium carbonate solution, *p*-nitroacetanilide and a small amount of 4 : 4′-dinitroazobenzene are formed. *Acetylchloroamino*-o-*chloro*-p-*nitrobenzene*, $NO_2 \cdot C_6H_3Cl \cdot NClAc$, forms light yellow prisms melting at 106°, and does not undergo intramolecular change under any conditions hitherto obtained. *Acetylchloroamino*-2 : 6-*dichloro*-4-*nitrobenzene* crystallises in pale yellow four-sided prisms, melting at 103°. *Acetylbromoamino*-p-*nitrobenzene* melts at 148°, and in acetic acid solution yields *p*-nitroacetanilide and *o*-bromo-*p*-nitroacetanilide, melting at 129°. *Acetylbromoamino*-o-*bromo*-p-*nitrobenzene* crystallises in light yellow twinned prisms which melt and decompose at 151°. As in the case of the corresponding chloro-derivative, it has not been found possible to bring about the intramolecular change of this compound. The 2 : 6-*dibromo*-compound melts and decomposes at 156°.

o-Chloro-*p*-nitroacetanilide is only formed in small quantity by the nitration of *o*-chloroacetanilide with a mixture of nitric and sulphuric acids, but is readily obtained by the use of fuming nitric acid at 0°. p-*Chloro*-o-*nitroacetanilide* crystallises in lustrous, yellow needles melting at 104°. *p*-Chloro-*m*-nitroacetanilide crystallises in long needles melting at 145°. A. H.

Molecular Rearrangement of Disubstituted Thioncarbamic Esters; Phenyliminothiocarbonic Acid Derivatives and Thiosemicarbazidic Esters. By HENRY L. WHEELER and GUY K. DUSTIN (*Amer. Chem. J.*, 1900, **24**, 424—444).—*Methyl methylthioncarbanilate*, $NPhMe \cdot CS \cdot OMe$, prepared by the action of sodium methoxide on methylthioncarbanilic chloride, is a colourless oil which boils at 151—152° under 19 mm. pressure; when an alcoholic solution of this compound is boiled with mercuric oxide, *methyl methylcarbanilate*, $NPhMe \cdot CO_2Me$, is obtained as an oil which distils at 117—119° under 16 mm. pressure. *Ethyl methylthioncarbanilate*, $NPhMe \cdot CS \cdot OEt$, is a colourless oil which boils at 145—150° under 18 mm. pressure and is not affected by boiling hydrochloric acid. *Methyl ethylthioncarbanilate*, $NPhEt \cdot CS \cdot OMe$, boils at 148—149° under 18 mm. pressure, crystallises from light petroleum in five-sided plates, and melts at 41—42°. Methyl methylthiolcarbanilate may be prepared by heating the corresponding thion ester with methyl iodide for four hours at 103—106°; it boils at 140—142° under 16 mm. pressure, crystallises from alcohol in colourless plates, and melts at 46°, not at 54° as stated by Bertram (Abstr., 1892, 466). *Ethyl methylthiolcarbanilate*, $\mathrm{NPhMe\cdot CO\cdot SEt}$, obtained by the action of ethyl iodide on the thion ester at 100°, boils at 160—163° under 19 mm. pressure, and melts at 12—13°. *Methyl ethylthiolcarbanilate*, $\mathrm{NPhEt\cdot CO\cdot SMe}$, boils at 148—149° under 17 mm. pressure.

When ethyl dithiocarbonate was left in contact with alcoholic dimethylamine for two weeks, the product was an oil boiling at 205—206°; estimation of the nitrogen indicated the presence of ethyl dimethylthioncarbamate. By the action of diamylamine on ethyl dithiocarbonate, mercaptan is evolved, but no other definite product could be isolated.

Dimethyl phenyliminothiolcarbonate, $\mathrm{NPh{:}C(SMe)\cdot OMe}$, obtained by the action of sodium methoxide and methyl iodide on methyl thioncarbanilate, is a yellow oil which boils at 133° under 17 mm. pressure, has a peculiar smell, and is converted by hydrogen chloride into methyl thiolcarbanilate; aniline reacts with this substance at 180—190°, carbanilide being produced, whilst methyl*iso*carbanilide is apparently not formed; di*iso*butylamine has very little action on it at 145—150°. This behaviour of methyl phenyliminothiolcarbonate with bases is in striking contrast with that of the derivatives of benzoyliminothiocarbonic acid, which react readily at a much lower temperature (Wheeler and Johnson, Abstr., 1900, i, 632). *Methyl benzoylthiolcarbanilate*, $\mathrm{NPhBz\cdot CO\cdot SMe}$, formed by heating methyl phenyliminothiolcarbonate with benzoyl chloride at 150°, crystallises in needles or prisms, and melts at about 93°. When methyl phenyliminothiolcarbonate is mixed with acetyl chloride, no action takes place, whilst ethyl phenyliminoformate reacts violently with acetyl chloride (Wheeler and Walden, Abstr., 1897, i, 280). *Methyl acetylthioncarbanilate*, $\mathrm{NPhAc\cdot CS\cdot OMe}$, prepared by the action of acetyl chloride on the silver salt of methyl thioncarbanilate, crystallises from dilute alcohol, melts at 47—49°, and when warmed with aniline yields methyl thioncarbanilate and acetanilide. Ethyl phenyliminothiolcarbonate boils at 157—160° under 21 mm. pressure, and is converted by hydrogen chloride into ethyl thiolcarbanilate. *Phenyliminothiol*iso*amylethylcarbonate*, $\mathrm{NPh{:}C(SC_5H_{11})\cdot OEt}$, obtained by the action of amyl bromide on the sodium salt of ethyl thioncarbanilate, decomposes on distillation under reduced pressure, and when heated with hydrogen chloride furnishes *iso*amyl thiolcarbanilate.

When ethyl phenylthioncarbazinate is warmed with acetyl thiocyanate, hydrogen sulphide is evolved, and a product is obtained which crystallises from alcohol in needles and melts at 93—94°; this *compound* is probably 4-acetyl-3-ethoxy-1-phenyl-5-thiotriazolone. Ethyl phenylthioncarbazinate reacts similarly with benzoyl thiocyanate to form a *compound*, which melts at 136—138°, and appears to be 4-benzoyl-3-ethoxy-1-phenyl-5-thiotriazolone. The last-mentioned substance is not changed when boiled with hydrochloric acid, ammonia, potassium hydroxide, aniline, or benzoyl chloride, but if heated with alcoholic silver nitrate, the sulphur is eliminated. *Ethyl* c-*acetylthio*-b-*phenyl*-a-*thiolsemicarbazidate*, $\mathrm{NHAc\cdot CS\cdot NPh\cdot NH\cdot CO\cdot SEt}$, obtained by the action of ethyl phenylthiolcarbazinate on acetyl thiocyanate, crystallises in prisms, melts at 145°, and is slightly soluble in benzene. *Ethyl* c-*benzoylthio*-b-*phenyl*-a-*thiolsemicarbazidate*,

$$\mathrm{NHBz\cdot CS\cdot NPh\cdot NH\cdot CO\cdot SEt},$$

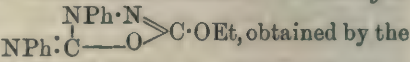
crystallises from benzene in colourless needles or prisms, and melts at 148—150°. *Ethyl* c : b-*diphenyl*-a-*thionsemicarbazidate*,

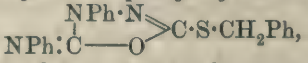
$$\mathrm{NHPh\cdot CO\cdot NPh\cdot NH\cdot CS\cdot OEt},$$

formed when ethyl phenylthioncarbazinate is warmed with phenyl carbimide, crystallises from alcohol in colourless prisms, melts at 114—115°, and, if heated with aniline, yields carbanilide. *Ethyl* c : b-*diphenyl*-a-*thiolsemicarbazidate*, $\mathrm{NHPh\cdot CO\cdot NPh\cdot NH\cdot CO\cdot SEt}$, obtained by the action of phenylcarbimide on the thiolcarbazinic ester, crystallises in plates, melts at 156°, and is very slightly soluble in alcohol. The corresponding *methyl* ester crystallises from alcohol in small plates, and melts and decomposes at 186°; it dissolves in sulphuric acid and is reprecipitated on the addition of water, and is not affected by boiling acetic anhydride; when its solution in alkali is boiled, a *compound* melting at 161° separates in needles. The *benzyl* ester crystallises in prisms or plates, melts at about 150°, and dissolves readily in benzene or hot alcohol, and sparingly in cold alcohol.

Methyl ethyl thiolcarbonate diphenylsemicarbazone,

$$\mathrm{NHPh\cdot CO\cdot NPh\cdot N{:}C(SMe)\cdot OEt},$$

obtained by the action of sodium methoxide and methyl iodide on ethyl diphenylthionsemicarbazidate, crystallises from alcohol, melts at 108—109°, and is converted by hydrogen chloride into methyl diphenylthiolsemicarbazidate. *Diethyl thiolcarbonate diphenylsemicarbazone*, $\mathrm{NHPh\cdot CO\cdot NPh\cdot N{:}C(SEt)\cdot OEt}$, crystallises from dilute alcohol in needles, melts at 111°, dissolves readily in alcohol or benzene, but only sparingly in light petroleum, and when treated with hydrogen chloride yields ethyl thiolsemicarbazidate. 5-*Ethoxy*-2-*phenylimino*-3-*phenyloxydiazoline*,  $\begin{matrix}\mathrm{NPh\cdot N} \\ | \\ \mathrm{NPh{:}C{-}{-}O}\end{matrix}\!\!>\mathrm{C\cdot OEt}$, obtained by the action of sodium ethoxide on ethyl *c*:*b*-diphenyl-*a*-thionsemicarbazidate, crystallises from alcohol in slender prisms, and melts at 86°. 5-*Benzylmercapto*-2-*phenylimino*-3-*phenyloxydiazoline*,



$$\begin{matrix}\mathrm{NPh\cdot N} \\ | \\ \mathrm{NPh{:}C{-}{-}O}\end{matrix}\!\!>\mathrm{C\cdot S\cdot CH_2Ph},$$

prepared by the action of benzyl chloride on a solution of ethyl diphenylthionsemicarbazidate in aqueous alkali, crystallises from alcohol in colourless needles, melts at 110—112°, and when heated with phosphorus pentachloride is decomposed.

When Bender's salt, $\mathrm{OEt\cdot CO\cdot SK}$, is treated with ethyl chlorocarbonate, carbon dioxide, carbon oxychloride, ethyl carbonate and ethyl thiolcarbonate are produced. Ethyl chlorocarbonate reacts with potassium xanthate with formation of carbon dioxide, carbon disulphide, ethyl carbonate, ethyl thioncarbonate, ethyl dithiocarbonate, and the compound, $\mathrm{S(CS\cdot OEt)_2}$, described by Welde (Abstr., 1877, 314). By the action of ethyl chlorocarbonate on ammonium dithiocarbanilate, carbon oxysulphide, carbanilide, and phenylthiocarbamide are obtained. The phenylhydrazine salt of dithiophenylcarbazinic acid reacts with ethyl chlorocarbonate in benzene solution with formation of ethyl phenylcarbazinate.

E. G.

Reaction of the Isomeric Acetylthiocarbamides with aqueous Sodium Hydroxide. By A. Hugershoff and W. Chr. König (*Ber.*, 1900, **33**, 3033—3035).—It has already been shown (Abstr., 1900, i, 156) that acetyl-phenylcarbamide and -*iso*phenylcarbamide are decomposed in different ways when heated with 33 per cent. aqueous sodium hydroxide on the water-bath. The first yields a thiocyanate and acetanilide, $NHPh{\cdot}CS{\cdot}NH{\cdot}COMe \rightarrow CN{\cdot}SH + NHPh{\cdot}COMe$, whilst the *iso*-compound yields phenylthiocarbamide and acetic acid, $NPh{:}C(SH){\cdot}N{:}CMe{\cdot}OH + H_2O \rightarrow NHPh{\cdot}CS{\cdot}NH_2 + CMeO{\cdot}OH$. The acetyl-α-naphthyl (following abstract) and acetyl-*o*-tolyl compounds behave in the same way. In the case of the acetyl-β-naphthyl- and acetyl-*p*-tolyl-thiocarbamides, however, the same products (thiocarbamides) are obtained as from the *iso*thiocarbamides; presumably the thiocarbamides were first transformed into the *iso*-compounds by the alkali. C. F. B.

Some Isomeric Acetylthiocarbamides of the Naphthalene Series. By A. Hugershoff and W. Chr. König (*Ber.*, 1900, **33**, 3029—3032).—Isomerism of the kind described in the case of thiocarbamides and *iso*thiocarbamides (Abstr., 1900, i, 155) had already been discovered by Freund and Hempel (Abstr., 1895, i, 193) in the case of tetrazole derivatives. In the transformation of the acetylthiocarbamides, it appears that a second hydrogen atom also changes its position, as is represented by the formulæ,

$$\underset{\text{Acetylphenylthiocarbamide.}}{NHPh{\cdot}CS{\cdot}NH{\cdot}COMe} \quad \text{and} \quad \underset{\text{Acetylphenyl}\textit{iso}\text{thiocarbamide.}}{NPh{:}C(SH){\cdot}N{:}CMe{\cdot}OH,}$$

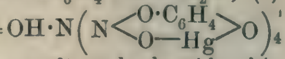
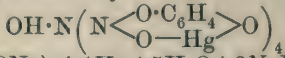
Some naphthyl derivatives have been prepared by the methods already described; these compounds, with their melting points, are: *Acetyl-α-naphthylthiocarbamide*, 146°; -*iso*thiocarbamide, 197°, already obtained by Miquel (*Bull. Soc. Chim.*, 1877, [ii], **28**, 103); *acetyl-β-naphthyl-thiocarbamide*, 145°; iso*thiocarbamide*, 158°. C. F. B.

Preparation of Pentachlorophenol. By Étienne Barral and L. Jambon (*Bull. Soc. Chim.*, 1900, [iii], **23**, 822—825).—Of the various methods which have been devised for the preparation of pentachlorophenol, the three most practical and economical are those in which phenol is chlorinated in the presence of antimony chloride (4—5 per cent.), iodine (2—3 per cent.), or anhydrous ferric chloride (3—4 per cent.), the last named reagent being, perhaps, the most efficient. The use of larger quantities than those stated causes the formation of resinous matters and of perchlorodioxydiphenylene, whilst if smaller quantities are employed the time required is increased although a purer product is obtained. It is important that the chlorine employed should be perfectly dry, in order to avoid the formation of tetrachloroquinone, that the temperature should not rise above 135—140°, and that the chlorinating agent should be added, not at the commencement of the operation, but only when the increase in weight observed corresponds with the conversion of the phenol into trichlorophenol. The crude product is washed with light petroleum, dissolved in sodium hydroxide, and 2—3 per cent. of sodium peroxide added; the pentachlorophenol is finally precipitated by adding a slight excess of hydrochloric acid, and crystallised from hot benzene.

N. L.

Some Pentachlorophenoxides. By L. Jambon (*Bull. Soc. Chim.*, 1900, [iii], **23**, 825—829).—The metallic pentachlorophenoxides may be obtained either by the direct action of pentachlorophenol on the metallic hydroxide or, in the case of the more insoluble compounds, by double decomposition. They are solid substances, generally crystallising in long needles or flattened prisms belonging to the orthorhombic system. The lead, silver, copper, and mercury compounds are insoluble in water, whilst the lithium and calcium derivatives are very soluble; all are insoluble in benzene or light petroleum. The pentachlorophenoxides are decomposed by acids, even by carbon dioxide, and when heated they yield a metallic chloride and perchlorodioxydiphenylene. The following compounds are described in the paper: C_6Cl_5OLi,H_2O; C_6Cl_5ONa,H_2O; C_6Cl_5OK,H_2O; $C_6Cl_5ONH_4,2H_2O$; $(C_6Cl_5O)_2Ca$; $(C_6Cl_5O)_2Sr,2H_2O$; $(C_6Cl_5O)_2Ba,2H_2O$; $(C_6Cl_5O)_2Mg,10H_2O$; $(C_6Cl_5O)_2Zn,H_2O$; $(C_6Cl_5O)_2Co,4H_2O$; $(C_6Cl_5O)_2Ni,8H_2O$; $(C_6Cl_5O)_2Cu,\frac{1}{2}H_2O$; $(C_6Cl_5O)_2Hg,2H_2O$; $(C_6Cl_5O)_2Pb$; C_6Cl_5OAg; $OH{\cdot}C_6H_5{\cdot}NH_2Ph$.

N. L.

Millon's Reaction. By Wilhelm Vaubel (*Zeit. angew. Chem.*, 1900, 1125—1130).—The author summarises the results he has obtained as follows: 1. The action of Millon's reagent (mercurous nitrate and nitric oxide) on phenol is represented by the following equations: (*a*) $2C_6H_5{\cdot}OH + 2NO + O = 2NO{\cdot}C_6H_4{\cdot}OH + H_2O$; (*b*) $NO{\cdot}C_6H_4{\cdot}OH + 4HgNO_3 + 3NO + 3C_6H_5{\cdot}OH =$  $OH{\cdot}N\left(N{<}\begin{smallmatrix}O{\cdot}C_6H_4\\O{-}Hg\end{smallmatrix}{>}O\right)_4$ $+ 3NO_2 + 3H_2O$. 2. On heating with aqueous sodium hydroxide this substance loses its mercury, and a reddish-brown soluble compound is formed which is precipitated by acids, the reaction being apparently as follows:  $OH{\cdot}N\left(N{<}\begin{smallmatrix}O{\cdot}C_6H_4\\O{-}Hg\end{smallmatrix}{>}O\right)_4$ $+ 9NaOH = ONa{\cdot}N(C_6H_4{\cdot}ONa)_2(O{\cdot}C_6H_4{\cdot}ONa)_2 + 4Hg + 5H_2O + 2NaNO_2 + 2NaNO_3$. 3. The compound thus obtained takes up with 4 atoms of bromine in the phenol groups and probably one also in place of the hydroxyl group, the substance $NBr(C_6H_3Br{\cdot}OH)_2(O{\cdot}C_6H_3Br{\cdot}OH)$ being thus formed. 4. Millon's reaction is not given by di-ortho and di-meta-substituted compounds. 5. Of the naphthols, only the β-compound yields a substance similar to that obtained from phenol. All the other naphthol derivatives investigated yielded nitroso-compounds.

L. de K.

A General Method for the Preparation of Mixed Phenyl Alkyl Carbonates; Pentachlorophenyl Alkyl Carbonates. By Étienne Barral (*Compt. rend.*, 1900, **131**, 679—681).—Many of the methods that might be expected to yield phenyl alkyl carbonates give unsatisfactory results, especially with substituted phenols, but good yields are obtained by the action of carbon oxychloride, dissolved in toluene, on a solution of the phenol in an excess of the alcohol to which an alkali hydroxide has been added in proportion equivalent to the phenol. In this way, the author has prepared several pentachlorophenyl alkyl carbonates; they are insoluble in water, but dissolve readily in organic solvents and are only slowly attacked by alkalis. *Pentachlorophenyl methyl carbonate* forms colourless needles melting at 137°; the corresponding *ethyl* ester forms large, colourless prisms melting at 66°; the *propyl* ester, small, micaceous crystals melting at 57°; the iso*propyl* ester, mamelons of small crystals which melt at 58°; the *butyl* ester, very large, colourless prisms melting at 59°; the iso*butyl* ester, very large, colourless, flattened prisms melting at 58°; the iso*amyl* ester, small needles melting at 54°; the *heptyl* ester, an oily liquid decomposed by heat; the *octyl* ester, an oily liquid very easily decomposed by heat; the *allyl* ester, small, white, nacreous, micaceous crystals melting at 57°; the *benzyl* ester, small, white needles melting at 116°. C. H. B.

Relation between the Constitution of Quinols and their Tendency to Form Quinones. By FRIEDRICH KEHRMANN (*Ber.*, 1900, **33**, 3066—3067).—Kauffmann has stated (Abstr., 1900, i, 480) that the fact that tetrachloroquinol is oxidised by trichloroquinone forms an exception to the author's rule (Abstr., 1898, i, 439). This is not the case, since the tetrachloroquinol has a higher molecular weight than trichloroquinol, and this more than counterbalances the effect of the fourth chlorine atom, which in aromatic compounds does not act as a very strongly negative radicle. A. H.

Energy of Non-carboxylic Organic Acids. By GIULIO COFFETTI (*Gazzetta*, 1900, **30**, ii, 235—246).—The energies of chloroanilic, bromoanilic, nitroanilic, leuconic, croconic, and rhodizonic acids have been determined, the first three by the sugar inversion method, and the others by measuring their electrical conductivities. Taking the energy of hydrochloric acid as 1, the energies of nitroanilic, bromoanilic, and chloroanilic acids have the values 0·684, 0·322, and 0·319 respectively. Croconic acid is a moderately strong acid, rhodizonic acid less so, whilst leuconic acid has very feeble acid properties. The results show that the accumulation of carbonyl groups in a molecule is not sufficient to increase its acidic energy, as much depends on the structural arrangement. The electro-negative energy given to a molecule by a carbonyl group seems to be less than that conferred by the entry of a chlorine or bromine atom or a nitro-group under the same conditions.

T. H. P.

Hydrolysis of Acid Amides. By EMMET REID (*Amer. Chem. J.*, 1900, **24**, 397—424. Compare Abstr., 1899, i, 507).—The author has continued his study of the hydrolysis of substituted benzamides, and has obtained results which are in accord with those previously published (*loc. cit.*).

The following values for the constant K have been obtained by means of dilute hydrochloric acid.

o-Phenoxybenzamide, *0·00562 and *0·00568; *o*-dimethylaminobenzamide, 0·00120; *o*-bromobenzamide, 0·00177; *p*-methoxybenzamide, 0·0131; *p*-ethoxybenzamide, 0·0185; *m*-hydroxybenzamide, 0·0114; *m*-iodobenzamide, *0·0189, and *p*-iodobenzamide, *0·0164.

The alkaline hydrolysis was effected by the aid of solution of barium hydroxide. The hydrochloric acid employed to estimate the ammonia produced was standardised in the following manner. A known weight of *p*-nitrobenzamide was treated with excess of solution of sodium hydroxide and distilled into a measured quantity of the acid. The author recommends this method for general use, since *p*-nitrobenzamide can be readily obtained in a pure state, and yields the calculated amount of ammonia when distilled with alkali. The following values for the constant *K* were obtained:

Benzamide........................ 0·0943

	Ortho.	Meta.	Para.
Toluamide	0·00508 0·00503	0·0780 0·0752	0·0623 0·0596
Nitrobenzamide	?	0·530	—
Chlorobenzamide	0·0435 0·0489	—	*0·180
Hydroxybenzamide	0·00616	0·0180	—
Bromobenzamide	0·0291	*0·282 0·273	*0·180
Iodobenzamide	0·0130	*0·245	*0·159
Methoxybenzamide	0·0528	—	0·0462
Ethoxybenzamide	0·0360	—	—
Dimethylaminobenzamide ...	0·0152	—	—
Phenoxybenzamide	*0·0427	—	—
Aminobenzamide	—	0·0877 0·0885	0·0178 0·0202

* These results were obtained when the concentration of the amide was half that employed in the other cases.

In the case of *o*-nitrobenzamide, anomalous results were obtained; in one series, the velocity decreased from 0·0522 (after ½ hour) to 0·0272 (after 4 hours). It was found that when *o*-nitrobenzamide is boiled with baryta water, it yields half the calculated amount of ammonia, and this quantity is not increased by prolonged boiling. The alkaline solution rapidly becomes red on heating, and, if acidified, a red, flaky precipitate is produced which is soluble in alcohol.

E. G.

Oxidation of Hippuric Acid to Carbamide. By ADOLF JOLLES (*Ber.*, 1900, **33**, 2834—2837. Compare Abstr., 1900, ii, 450—454).—Glycine is not acted on by permanganate in acid solution, but is readily oxidised by it in alkaline solution. Creatinine, similarly, is not oxidised by the acid reagent, whereas ethyl aminoacetate is immediately oxidised. The author attributes this to the closed ring constitutions of glycine and creatinine, and the open chain constitution of the ester and alkali salts of the former.

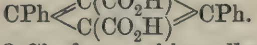
When hippuric acid is boiled with acid permanganate, in other words, when glycine is oxidised at the moment of formation, a theoretical yield of carbamide is obtained.

J. J. S.

Condensation of α-Bromo*allo*cinnamic Acid. By W. Manthey (*Ber.*, 1900, **33**, 3081—3086).—The author has already shown (Abstr., 1899, i, 894) that the product obtained by the action of sulphuric acid on α-bromo*allo*cinnamic acid has the formula $(C_9H_5OBr)_x$, and not $C_7H_{12}O_2Br_2$, as supposed by Leuckart (Abstr., 1882, 615). On reduction with platinised zinc dust and acetic acid, it yields a mixture of *truxone* and *dihydrotruxone*, $(C_9H_8O)_x$; the latter is identical with Leuckart's reduction product and is converted by oxidising agents into truxone.

Estimations of the molecular weight of dihydrotruxone in boiling benzene or acetone show that it has the formula $C_{18}H_{16}O_2$, from which it may also be inferred that truxone is $C_{18}H_{18}O_2$, contrary to the view taken by Liebermann; this confirms the opinion expressed by Kipping (Trans., 1894, **65**, 975).

Determinations of the molecular weight of triphenyltrimesic acid and its ethyl esters indicate that this acid also has the bimolecular formula $C_{18}H_{12}O_4$, and the molecular conductivity of its sodium salt is in accordance with this conclusion; $\mu 1024 - \mu\ 32 = 21{\cdot}07$, which is approximately the number characteristic of dibasic acids. The acid is therefore, in reality, diphenyl*cyclo*butenedicarboxylic acid,



$$CPh\Big<\begin{matrix}C(CO_2H)\\C(CO_2H)\end{matrix}\Big>CPh.$$

Chlorotruxone, $C_{18}H_{10}O_2Cl_2$, from α-chloro*allo*cinnamic acid, separates from xylene in white, cubic crystals, is sparingly soluble in the ordinary media, and melts and decomposes at 290°. A. L.

Sulphonic Derivatives of Methyl-*p*-amino-*m*-hydroxybenzoate (Orthoform). By Paul Jacob (*J. Pharm.*, 1900, [vi], **12**, 210—217) —When methyl *p*-amino-*m*-hydroxybenzoate is dissolved in sulphuric acid, a dark green coloration is produced, whereas the corresponding *m*-amino-derivative, on similar treatment, gives a red coloration.

Methyl hydrogen p-*amino*-m-*hydroxysulphobenzoate*,

$$SO_3H{\cdot}C_6H_2(OH)(NH_2){\cdot}CO_2Me,$$

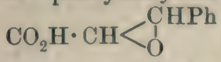
obtained by the action of fuming sulphuric acid, crystallises, with $3H_2O$, in slender needles which melt at 208—209°, and is very readily soluble in water or alcohol. The sodium, calcium, barium, zinc, and copper salts of the monomethyl ester were prepared.

H. R. Le S.

Presence of Homologous Coumarones in Coal-tar. By Richard Stoermer and Johannes Boes (*Ber.*, 1900, **33**, 3013—3020).— A fraction of coal-tar boiling at 185—195° was shaken with sulphuric acid, poured into water, extracted with ether, and the product separated from volatile hydrocarbons by a current of superheated steam. Subsequent dry distillation gave a neutral oil consisting of hydrindene, methylcoumarones, and substances of higher boiling point, together with a phenolic mixture containing *o*-, *m*-, and *p*-cresols. From these observations, the presence of 6-, 5- or 3-, and 4-methylcoumarones in the tar is deduced.

A fraction boiling at 215—225°, when treated in a similar way, gave a product which was identified as 4 : 6-dimethylcoumarone, whilst the phenolic part of the distillate consisted of *as-m*-xylenol.

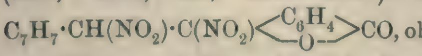
T. M. L.

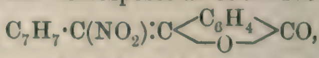
Partial Conversion of 'Phenyloxyacrylic Acid' into Phenylpyruvic Acid. By EMIL ERLENMEYER, jun. (*Ber.*, 1900, **33**, 3001—3002. Compare Abstr., 1891, 1482).—The constitution of phenylethylene-oxide-carboxylic acid (phenyloxyacrylic acid),  $CO_2H\cdot CH<\begin{matrix}CHPh\\|\\O\end{matrix}$, is confirmed by its partial conversion into phenylpyruvic acid, when heated with hydrochloric acid; this change is analogous to the conversion of phenylethylene oxide into phenylacetaldehyde (Breuer and Zincke, Abstr., 1878, 886). T. M. L.

Esterification of Unsymmetrical Di- and Poly-basic Acids. III. Esterification of 3- and 4-Nitrophthalic Acid. By RUDOLF WEGSCHEIDER and ALFRED LIPSCHITZ (*Monatsh.*, 1900, **21**, 787—812. Compare Abstr., 1900, i, 657, 658).—The *monomethyl* ester of 3-nitrophthalic acid, in which the free carboxyl group occupies the 1-position, that is, the α-compound according to the nomenclature of Wegscheider (*Monatsh.*, **16**, 139), crystallises with H_2O, melts, when anhydrous, at 144—145°, has a conductivity $K = 0{\cdot}2$, and is obtained by any of the following methods:—the partial hydrolysis of the diethyl ester; the action of methyl iodide on the *potassium hydrogen* salt, which crystallises, with $1\frac{1}{2}H_2O$, in long, slender, silky needles; the action of methyl alcohol on the anhydride, and the action of methyl alcohol on the free acid in the absence of strong mineral acids. The *β-monomethyl ester* crystallises in pale yellow tablets, melts at 157—158°, has a conductivity $K = 1{\cdot}5$, and is obtained by the action of methyl alcohol on the acid in the presence of hydrochloric or sulphuric acids, it differs from the α-ester in giving no precipitate with solutions of ferric chloride, lead acetate, or alum.

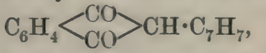
When 4-nitrophthalic acid is subjected to all the above methods of esterification, only the diethyl ester and one monomethyl ester are obtained; this *monomethyl ester* crystallises with H_2O and melts at 129°. *Potassium hydrogen 4-nitrophthalate* crystallises with H_2O.

R. H. P.

Derivatives of *o*-Xylylidenephthalide. By PAUL GOLDBERG (*Ber.*, 1899, **33**, 2818—2824).—*o-Xylylidenephthalide dinitrite*,  $C_7H_7\cdot CH(NO_2)\cdot C(NO_2)<\begin{matrix}C_6H_4\\O\end{matrix}>CO$, obtained by adding liquid nitrogen peroxide to *o*-xylylidenephthalide dissolved in cooled benzene or acetic acid, is crystalline and melts and decomposes at 158—159°.

Nitro-o-xylylidenephthalide,  $C_7H_7\cdot C(NO_2){:}C<\begin{matrix}C_6H_4\\O\end{matrix}>CO$, produced by warming the foregoing compound with moist amyl alcohol, forms beautiful, lemon-yellow crystals melting at 167—169°. The *sodium* derivative, $C_{16}H_{11}O_5NNa_2,2H_2O$, forms white crystals which become yellow at 80°.

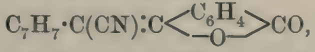
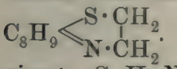
On dissolving nitroxylylidenephthalide in sodium hydroxide and saturating the solution with oxalic acid, phthalic anhydride crystallises out and *a-tolylnitromethane*, $C_6H_4Me\cdot CH_2\cdot NO_2$, remains in solution, and may be separated by distillation in a current of steam. This substance dissolves in aqueous sodium hydroxide, and on adding acid to the solution, the iso*nitro*-derivative is precipitated as a white, crystalline substance, which slowly reverts to the normal form.

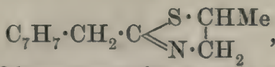
2-o-*Tolyldiketohydrindene*,  $C_6H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}CH\cdot C_7H_7$, formed when *o*-xylylidenephthalide is boiled with a solution of sodium methoxide, separates from boiling alcohol in beautiful, yellowish crystals melting at 179—180°. The *dioxime*, $C_{16}H_{12}(NOH)_2$, crystallises from alcohol and melts at 212°. The *phenylhydrazone*, $C_{16}H_{12}O\cdot N_2HPh$, forms yellow crystals melting at 173—174°.

2-o-*Tolyl-2-methyldiketohydrindene*, $C_6H_4{:}(CO)_2{:}CMe\cdot C_7H_7$, prepared from tolyldiketohydrindene by treatment with sodium methoxide and methyl iodide, is a yellow crystalline substance melting at 149°. The corresponding *ethyl*, *benzyl*, and *benzoyl* derivatives melt at 179°, 179°, and 181° respectively.

Bromo-2-o-tolyldiketohydrindene, $C_{16}H_{11}O_2Br$, separates from alcohol in yellow crystals and melts at 171—172°. *Dichloro-2-o-tolyldiketohydrindene*, $C_{16}H_{10}O_2Cl_2$ melts at 125·5°.

Nitro-o-tolyldiketohydrindene, $C_{16}H_{11}O_2\cdot NO_2$, obtained by the action of nitrogen peroxide on *o*-tolyldiketohydrindene, forms white crystals melting at 131°. By using fuming nitric acid, a *dinitro*-derivative $C_{16}H_{10}O_2(NO_2)_2$ melting at 159—160° is obtained.

o-*Cyano-o-xylylidenephthalide*,  $C_7H_7\cdot C(CN){:}C{<}\begin{smallmatrix}C_6H_4\\-O-\end{smallmatrix}{>}CO$, formed when *o*-tolylacetonitrile and phthalic anhydride are heated at 240—245° with a little anhydrous sodium acetate, melts at 191—192°. *o*-Tolylthioacetamide, $C_7H_7\cdot CH_2\cdot CS\cdot NH_2$, melts at 115°, and when heated with ethylene dibromide, is converted into o-*xylylthiazoline*,  $C_8H_9{<}\begin{smallmatrix}S\cdot CH_2\\ \mid\\ N\cdot CH_2\end{smallmatrix}$. The latter is oily, but yields a sparingly soluble *picrate*, $C_{11}H_{13}NS,C_6H_3O_7N_3$, melting at 154—155°, and a *platinichloride*, $(C_{11}H_{13}NS)_2,H_2PtCl_6$, which forms beautiful, yellow crystals melting at 191°.

5-*Methyl*-2-o-*xylylthiazoline*,  $C_7H_7\cdot CH_2\cdot C{<}\begin{smallmatrix}S\cdot CHMe\\ \mid\\ N\cdot CH_2\end{smallmatrix}$, prepared from *o*-tolylthioacetamide and β-bromopropylamine, is a yellow oil with an odour resembling that of coniine, and gives a sparingly soluble *picrate*, $C_{12}H_{15}NS,C_6H_3O_7N_3$, melting at 126° and a *platinichloride*, $(C_{12}H_{15}NS)_2,H_2PtCl_6$, melting at 156—157°. A. L.

Explanation of Tautomeric Phenomena. By PAUL RABE (*Annalen*, 1900, **313**, 129—207. Compare Knorr, Abstr., 1899, i, 673).—The preliminary portion of the paper is devoted to a discussion of earlier memoirs dealing with the subject of tautomerism, and contains a useful summary of existing information relating to this phenomenon. With the object of studying the conditions which influence the stability of the desmotropic forms of a tautomeric substance, the author has investigated the various modifications of ethyl benzylidenebisacetoacetate and of ethyl methylenebisacetoacetate.

No fewer than twenty-two modifications of ethyl benzylidenebisacetoacetate are theoretically possible, this number being composed of five double ketonic esters, $CHPh(CHAc\cdot CO_2Et)_2$, twelve half enolic esters, $CO_2Et\cdot CHAc\cdot CHPh\cdot C(CO_2Et)\colon CMe\cdot OH$, and five double enolic esters, $CHPh[C(CO_2Et)\colon CMe\cdot OH]_2$, and of these, three double ketonic esters (β-esters) and three half enolic esters (α-esters) have been characterised.

When ethyl benzylidenebisacetoacetate is prepared by Knoevenagel's method (Abstr., 1895, i, 48), namely, by condensing benzaldehyde with ethyl acetoacetate (2 mols.) under the influence of piperidine, three different esters are produced; they do not give directly a coloration with ferric chloride, and must be therefore regarded as double ketonic esters. The β_1-ester is the chief product, being the compound described already by Hantzsch (Abstr., 1886, 77); it crystallises from alcohol in slender needles, and melts at 149—150°. The *β_2-ester* forms a small proportion of the mixture, and crystallises from alcohol in rhombs melting at 154°. The *β_3-ester* occurs in very small quantities, and crystallises from dilute alcohol in prismatic needles which contain $2H_2O$ and melt at 90—93°; the anhydrous substance melts at 107—108°.

On treating the β_1-ester with sodium ethoxide, even when the latter is in excess, there is produced the *sodium* derivative of the α_1-ester, $C_{19}H_{23}O_6Na$, which crystallises in leaflets containing 1 mol. of alcohol, and melts at 132—135°, when it decomposes. When water acts on this salt, the β_1-ester is regenerated, but sulphuric acid liberates the *α_1-ester*, which crystallises in small prisms containing $1H_2O$, and melting at 68—70°; if maintained at the melting point, it becomes transformed into the β_1-ester, but when the temperature is rapidly raised, water is removed at 100°, and the fused mass solidifies, afterwards melting at 148—150°, the melting point of the β_1-ester. The α_1-ester develops an intense reddish-violet coloration with ferric chloride, and is therefore the half-enolic modification; the hydrated substance becomes anhydrous when the solution in absolute ether, is agitated with anhydrous sodium sulphate, and in this condition melts at 60°.

The *α_2-ester*, prepared in the same way from the β_2-ester, is a transparent, viscous oil which gradually solidifies, regenerating the β_2-ester; the *sodium* derivative crystallises in orange coloured, hygroscopic leaflets, which evolve gas and melt to a viscous liquid at 90—100°. The *α_3-ester* melts at 65—67°.

The experiments described by Schiff (Abstr., 1899, i, 366) suggest that the β-esters are interconvertible, but the author has found that this is not the case, and that Schiff's putative isomerides melting at 134—135° and 120° are merely mixtures.

Knorr (*loc. cit.*) has studied the conditions of equilibrium obtaining among the isomeric ethyl diacetylsuccinates, and found that it is from the proportion of isomerides in fused mixtures only that conclusions regarding their relative stability can be drawn, the proportion in the case of dissolved mixtures being too dependent on the nature of the solvent. As in the series investigated by Knorr, the stability limits of the ethyl benzylidenebisacetoacetates appear to coincide with their melting points, but in the case of the α_2-ester this statement cannot be made with certainty. Both in the fused and dissolved states, the esters yield allelotropic mixtures, consisting in each case of the β-ester associated with the corresponding α-compound. M. O. F.

Bis-*p*-dimethyl-*o*-carboxycinnamic and Bisdimethylphthalic Acids from the Oxidation of Bisdihydrosantinic Acid. By GIUSEPPE GRASSI-CRISTALDI and G. TOMARCHIO (*Gazzetta*, 1900, **30**, ii, 122—127).—The oxidation of bisdihydrosantinic acid by means of 4 per cent. permanganate solution yields the following two acids.

Bis-p-*dimethyl*-o-*carboxycinnamic acid*, $C_{22}H_{24}O_8$, gives a *barium* salt which is soluble and a *silver* salt insoluble in water.

Bis-p-*dimethylphthalic acid*, $C_{20}H_{18}O_8$, which is also obtained by oxidation of the former compound, yields a *barium* salt insoluble in water. T. H. P.

Iodine Derivatives of [Acetophenone]. By A. COLLET (*Bull. Soc. Chim.*, 1900, [iii], **23**, 829—832. Compare Abstr., 1899, i, 434).—The following iodine derivatives of acetophenone have been prepared by warming alcoholic solutions of the corresponding chlorine or bromine compounds with potassium iodide at 60—70°.

p-*Chlorophenyl iodomethyl ketone*, $C_6H_4Cl\cdot CO\cdot CH_2I$, crystallises in colourless, silky needles melting at 75·5°; on oxidation with potassium permanganate in alkaline solution, it yields *p*-chlorobenzoic acid.

p-*Bromophenyl iodomethyl ketone*, $C_6H_4Br\cdot CO\cdot CH_2I$, crystallises in white needles melting at 90° and yields *p*-bromobenzoic acid when oxidised with alkaline potassium permanganate.

Phenyl diiodomethyl ketone, $COPh\cdot CHI_2$, was obtained as a heavy, brown, oily liquid which boils and decomposes above 200° and yields benzoic acid on oxidation.

p-*Chlorophenyl diiodomethyl ketone*, $C_6H_4Cl\cdot CO\cdot CHI_2$, forms small, colourless crystals melting at 111—112° and yields *p*-chlorobenzoic acid on oxidation.

p-*Bromophenyl diiodomethyl ketone*, forms colourless crystals which melt at 119—120° and when oxidised yields *p*-bromobenzoic acid.

Phenyl triiodomethyl ketone, $COPh\cdot CI_3$, is a heavy, brown, oily liquid which decomposes when heated and yields benzoic acid on oxidation.

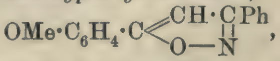
The compounds described above are all insoluble in water, but more or less soluble in the usual organic solvents; they are quickly decomposed on exposure to light, iodine being liberated, and their vapours strongly irritate the eyes. N. L.

Action of Sodium Methoxide on Anisylidene Acetophenone Dibromide. By F. J. POND and ARTHUR S. SHOFFSTALL (*J. Amer. Chem. Soc.*, 1900, **22**, 658—685. Compare Abstr., 1900, i, 102, and Wislicenus, *ibid.*, i, 37).—Anisylideneacetophenone dibromide separates from ethyl acetate in large crystals melting at 139—140°, but when boiled for a short time with alcohol yields an additive compound of *bromoanisylideneacetophenone* and *ethyl alcohol*,

$$OMe\cdot C_6H_4\cdot CHBr\cdot CH(OEt)\cdot COPh$$

or $OMe\cdot C_6H_4\cdot CH(OEt)\cdot CHBr\cdot COPh$; this melts at 73·5—74·5°, and when carefully heated at 155—160° evolves ethyl alcohol and yields *bromoanisylideneacetophenone*, which crystallises from ethyl acetate in large plates melting at 94·5°. The additive compound with methyl alcohol crystallises in colourless needles melting at 102°, and the compound with propyl alcohol is an oil.

The substance melting at 131—132°, previously described as benzoylanisoylmethane, is now shown to be *α-hydroxyanisylideneacetophenone*, $OMe\cdot C_6H_4\cdot C(OH):CH\cdot COPh$, the *copper* derivative, $C_{32}H_{26}O_6Cu$, forms small, pale green needles melting and decomposing at 247—249°, and when warmed with dilute hydrochloric acid regenerates the pure hydroxyketone. Hydroxylamine hydrochloride reacts with an alcoholic solution of α-hydroxyanisylideneacetophenone, yielding *3-phenyl-5-p-methoxyphenyl*iso*oxazole*,



$$OMe\cdot C_6H_4\cdot C\left\langle\begin{array}{l} CH\cdot CPh \\ \quad\ \ \| \\ O\text{—}N \end{array}\right.,$$

which crystallises in pearly flakes melting at 120°, and is insoluble in water or alkalis. An isomeric *phenyl-p-methoxyphenyl*iso*oxazole* obtained when anisylideneacetophenone dibromide is treated with hydroxylamine hydrochloride and an excess of potash, crystallises in slender needles melting at 127—128°, and is soluble in most organic solvents. Bromine reacts with a chloroform solution of α-hydroxyanisylideneacetophenone, yielding *benzoylanisoylbromomethane*,

$$OMe\cdot C_6H_4\cdot CO\cdot CHBr\cdot COPh,$$

which melts at 128°; it dissolves in most organic solvents, and its alcoholic solution is not coloured by ferric chloride.

In the preparation of α-hydroxyanisylideneacetophenone, a small amount of a compound melting at 90° is always obtained, which probably has the constitution $OMe\cdot C_6H_4\cdot CH(OH)\cdot CH(OH)\cdot COPh$.

The first product of the action of sodium ethoxide on anisylideneacetophenone dibromide is a heavy oil, probably *α-ethoxyanisylideneacetophenone*, which on treatment with dilute acids is hydrolysed to α-hydroxyanisylideneacetophenone.

The same hydroxy-compound is also formed when α-bromoanisylideneacetophenone is treated first with sodium methoxide or ethoxide and then with dilute acids. J. J. S.

Chemical Action of Light. By GIACOMO L. CIAMICIAN and PAUL G. SILBER (*Ber.*, 1900, **33**, 2911—2913).—The product obtained by the action of light on a mixture of alcohol and benzophenone (Oechsner de Coninck and Devrien, Abstr., 1900, i, 502) is Linnemann's benzopinacone, $OH\cdot CPh_2\cdot CPh_2\cdot OH$ (*Annalen*, 1865, **133**, 26), and the product from alcohol and acetophenone is acetophenonepinacone, $OH\cdot CMePh\cdot CMePh\cdot OH$. T. M. L.

Derivatives of Benzophenone. V and VI. By PIETRO BARTOLOTTI (*Gazzetta*, 1900, **30**, ii, 224—229 and 229—234. Compare Abstr., 1899, i, 368).—*Benzoyl-*m*-tolyl benzoate*, $C_6H_3MeBz\cdot OBz$, prepared by heating *m*-tolyl benzoate with benzoyl chloride in presence of zinc chloride, crystallises from alcohol in silky, white needles melting at 104—105° and is soluble in the ordinary solvents, but insoluble in sodium hydroxide. On hydrolysis with alcoholic sodium hydroxide, it yields benzoyl-*m*-cresol.

*Benzoyl-*m*-cresol*, $C_6H_3MeBz\cdot OH$, separates from a mixture of benzene and light petroleum in small, colourless crystals melting at

128°, and is soluble in sodium hydroxide solution, giving a yellow liquid, and also in the ordinary solvents. *Benzoyl-*m*-tolyl acetate*, $C_6H_3MeBz\cdot OAc$, is an almost colourless liquid soluble in the ordinary solvents, but insoluble in sodium hydroxide solution.

*Benzoyl-*m*-tolyl methyl ether*, $C_6H_3MeBz\cdot OMe$, obtained by heating benzoyl *m*-cresol with methyl alcoholic potassium hydroxide and methyl iodide, is a dense, colourless liquid very soluble in the ordinary solvents, but insoluble in sodium hydroxide solution.

*Benzoyl-*o*-tolyl benzoate*, prepared similarly to the *m*-compound, separates from alcohol in white, silky crystals melting at 99·5°, and is soluble in the ordinary solvents, but insoluble in sodium hydroxide solution.

*Benzoyl-*o*-cresol*, obtained by hydrolysing the previous compound, is deposited from alcohol in white, silky crystals which melt at 172—172·5° and dissolve in the ordinary solvents, and in sodium hydroxide solution. *Benzoyl-*o*-tolyl acetate* is a dense, pale yellow liquid insoluble in sodium hydroxide, but soluble in the ordinary solvents.
T. H. P.

The Ketones of Anthracene. By EDUARD LIPPMANN and PAUL KEPPICH (*Ber.*, 1900, **33**, 3086—3092).—When a solution of benzoyl chloride and anthracene in carbon disulphide is heated with freshly-prepared aluminium chloride, a crystalline, apparently homogeneous product, melting at 158—160°, is produced, whilst, if the aluminium chloride has been allowed to absorb a small quantity of moisture, a large quantity of pure anthraphenone melting at 148° is readily obtained. Investigation of the product of higher melting point has shown that it may be produced by crystallising anthraphenone with 3 per cent. of anthracene.

Anthraphenone, $C_{14}H_9\cdot COPh$, crystallises from ethyl acetate in needles melting at 148°. The crystals belong to the monoclinic system $[a:b:c=1\cdot1704:1:0\cdot8623;\ \beta=94^\circ34']$. On oxidation with a mixture of chromic and acetic acid, it is converted into anthraquinone and benzoic acid.

Dihydroanthraphenone, $C_{14}H_{11}\cdot COPh$, made by reducing anthraphenone with zinc dust and acetic acid, crystallises from alcohol in lustrous, white needles melting at 101°. It rapidly reduces an ammoniacal solution of silver nitrate and is oxidised by chromic acid, yielding anthraquinone. It does not yield an acetyl or benzoyl derivative, and is therefore benzoyldihydroanthracene.

Nitroanthraphenone, $C_{21}H_{13}O\cdot NO_2$, crystallises from alcohol in golden-yellow needles having a metallic lustre and melting at 174°. It gives anthraquinone on oxidation, and dihydroanthraphenone and ammonia on reduction.

Tribenzoylanthracene, $C_{14}H_7Bz_3$, a bye-product in the preparation of anthraphenone, separates from nitrobenzene in yellow crystals which melt above 300°, and produces a dark red coloration with sulphuric acid. With chromic acid, it is converted into a substance which resembles anthraquinone, but melts at 255—256°; with excess of chromic acid, it gives anthraquinone and benzoic acid.

Tribenzoyltetrahydroanthracene, $C_{14}H_{11}Bz_3$, prepared by prolonged action of zinc dust and acetic acid on tribenzoylanthracene, forms yellow prisms melting at 187—188°. It does not react with acetic anhydride at high temperatures in closed tubes, so that in this substance also the carbonyl groups are intact. It reduces ammoniacal silver solutions, and is oxidised by chromic acid, yielding anthraquinone and benzoic acid.

A. L.

Thujene, a New Dicyclic Terpene. By L. Tschugaeff (*Ber.*, 1900, **33**, 3118—3126).—On converting thujyl alcohol into the corresponding methyl xanthate and subjecting the latter to dry distillation (compare Abstr., 1900, i, 129 and 352), *thujene*, $C_{10}H_{16}$, is obtained which boils at 151—152·5°, and has a sp. gr. 0·8275 at 20°/4° and n_D 1·45042 at 20°; the molecular refraction is 44·21, the calculated value for a dicyclic terpene being 43·54. It fails to yield a crystalline nitrosochloride, and with bromine (1 mol.) gives rise to hydrogen bromide and a reddish-brown syrup, which dissolves in alcohol with an intensely red colour. When exposed to the air, thujene is rapidly oxidised to a resin, whilst it decolorises aqueous potassium permanganate instantaneously; with hot mercuric acetate solution it yields a crystalline *substance* having a nacreous lustre.

From physical considerations, the new terpene appears to belong to the true thujone series, thujone itself probably having the structure assigned to it by Semmler (Abstr., 1900, i, 240); the terpene hitherto called "tanacetene" or "thujene" (Semmler, Abstr., 1893, i, 107; Wallach, *ibid.*, i, 106) probably corresponds with *iso*thujone and is therefore named iso*thujene* (compare Wallach, Abstr., 1895, i, 620).

W. A. D.

Formation of Terpene Derivatives in the Geranium. By Eugène Charabot (*Compt. rend.*, 1900, **131**, 806—808. Compare Abstr., 1899, i, 299; 1900, i, 241, 303; ii, 101, 361, 362).—The alcohols present in the essential oil of geranium are geraniol and rhodinol.

Two samples of the oil were obtained from the green plant, the second sample being collected one month after the first, and gave the following numbers:

	I.	II.
Sp. gr. at 15°	0·897	0·899
Rotatory power (l = 100 mm.)	−10°	−10°16′
Coefficient of saturation of the acids	43·8 per cent.	41·0 per cent.
Esters (calc. as geranyl tiglate)	5·8 ,,	10·0 ,,
Free alcohol (calc. as $C_{10}H_{18}O$)	64·0 ,,	62·1 ,,
Total alcohol	67·8 ,,	68·6 ,,

The acidity and the amount of free alcohol diminish, whereas the amount of esters and total alcohol increase, during the maturation of the plant. Estimation of the amount of menthol present at different stages in the growth of the plant showed that this substance is chiefly formed in the period during which the plant possesses maximum respiratory activity.

H. R. Le S.

Neroli Oil. By HEINRICH WALBAUM (*Ber.*, 1900, **33**, 2994. Compare Abstr., 1899, i, 620, 621).—Priority is still claimed over E. and H. Erdmann (Abstr., 1900, i, 555). J. J. S.

Occurrence of Phenylethyl Alcohol in Oil of Roses. By HUGO VON SODEN and WILHELM ROJAHN (*Ber.*, 1900, **33**, 3063—3065. Compare Abstr., 1900, i, 489).—The authors point out that their discovery of the occurrence of phenlethyl alcohol in oil of roses was published before that of Walbaum (Abstr., 1900, i, 645). The investigation of two samples of French oil of roses prepared from the fresh flowers shows that 25—45 per cent. of the ethereal oil present consists of this alcohol. A small amount of the alcohol has also been found in Bulgarian oil of roses. A. H.

A New Glucoside Extracted from the Seeds of Erysimum, a Member of the Cruciferæ. By FRÉDÉRIC SCHLAGDENHAUFFEN and E. REEB (*Compt. rend.*, 1900, **131**, 753—755).—The seeds of *Erysimum aureum* contain an alkaloid which causes paralysis when injected into animals and also a glucoside, erysimin, which resembles digitalin in its action on the heart. *Erysimin*, $C_4H_7O_2$, is a pale yellow, slightly hygroscopic, amorphous powder which melts at 190° and is soluble in all proportions in water and alcohol, but insoluble in ether, chloroform, benzene, or carbon disulphide. It affords the usual reactions of a glucoside. N. L.

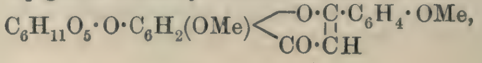
Active Glucosides Soluble in Water contained in Frangula, Sagrada and Rhubarb. By EUGEN AWENG (*Chem. Centr.*, 1900, ii, 766—767; from *Apoth.-Zeit.*, **15**, 537—538).—*Frangula, Sagrada*, and rhubarb contain two groups of active components, consisting respectively of primary glucosides easily soluble in water and of secondary glucosides which are only slightly so. The latter are isolated by treating the residue obtained by evaporating the 70 per cent. alcoholic extract with ammonia and precipitating with acetic acid. The filtrate in each case contains the same primary glucosides, frangulic acid and a glucoside which on hydrolysis yields emodin; these compounds are easily separated by means of 96 per cent. alcohol. The emodin glucoside is almost completely precipitated from its aqueous solution by baryta, gelatin solution or formalin. Frangulic acid, from *Frangula, Sagrada*, or rhubarb, dissolves in ammonia, forming a yellow solution whilst the emodin glucoside yields an intense raspberry-red solution. The precipitate with formalin might be used to locate microscopically the position of the glucoside in the rhubarb rhizome. *Radix Rhapontici* was found to contain the same glucosides as rhubarb. The emodin glucoside is more active than frangulic acid. Since the secondary glucosides of rhubarb are partly soluble in hot water and on cooling separate out again, infusion of rhubarb should be filtered hot. E. W. W.

Nature and Origin of the Poison of Lotus Arabicus. By WYNDHAM R. DUNSTAN and THOMAS A. HENRY (*Proc. Roy. Soc.*, 1900, **67**, 224—226).—*Lotus Arabicus*, a leguminous plant indigenous to Egypt and Northern Africa, contains in its leaves a yellow, crystalline glucoside, *lotusin*, $C_{22}H_{19}O_{10}N$, which under the influence of an enzyme, *lotase*, also found in the plant, is hydrolysed into hydrogen cyanide, dextrose, and a new yellow colouring matter, *lotoflavin*, $C_{15}H_{10}O_6$. The coloured product belongs to the class of phenylated pheno-γ-pyrones, and is a dihydroxychrysin isomeric with luteolin and fisetin obtained respectively from *Reseda luteola* and *Rhus cotinus*.

Lotusin and amygdalin are the only glucosides definitely known to yield hydrocyanic acid on hydrolysis. G. T. M.

Apiin. By Eduard Vongerichten (*Ber.*, 1900, **33**, 2904—2909).—*Apiin methyl ether*, $C_{28}H_{30}O_{14},2H_2O$, prepared by the action of methyl iodide and sodium methoxide on apiin, is a somewhat ill-defined product which crystallises from dilute alcohol, melts between 185° and 200°, and does not reduce Fehling's solution. It is hydrolysed by dilute hydrochloric acid to *apigenin methyl ether*, $C_{16}H_{12}O_5$, which crystallises from alcohol in minute needles and melts at 256—257°; the *diacetyl* derivative forms white needles and melts at 198—200°; the ether is hydrolysed by potassium hydroxide into anisic acid and phloroglucinol.

By acting on apiin with aqueous potassium hydroxide and methyl iodide, a new *glucoside* is also produced which crystallises from dilute alcohol in white needles and melts at 255°; it is regarded as a derivative of apigenin dimethyl ether, and the formula



$$C_6H_{11}O_5\cdot O\cdot C_6H_2(OMe)<\begin{array}{l}O\cdot C\cdot C_6H_4\cdot OMe,\\ \quad\;\, \| \\ CO\cdot CH\end{array}$$

is suggested. T. M. L.

Bitter Principles of Hops. By Georg Barth (*Chem. Centr.*, 1900, ii, 915—916; from *Zeit. ges. Brauw.*, **23**, 537—542. Compare Abstr., 1900, ii, 746).—Lupulinic acid, $C_{25}H_{26}O_4$, is identical with H. Bungener's lupulinic acid, to which, however, the incorrect formula $C_{50}H_{70}O_8$ is ascribed and also with Lermer's β-bitter acid. Vlaandern's resin, $C_{54}H_{35}O_{11}\cdot OH$, obtained by precipitating the alcoholic hop extract with water, is identical with the β-resin. When lupulinic acid is oxidised by potassium permanganate, it forms valeric acid and when heated with iodine in alkaline solution it yields iodoform. The latter reaction indicates the presence of a methoxyl group and its power of combining with bromine proves the acid to contain at least two double linkings; in Hübl's iodine addition method probably substitution also occurs. The acid character of lupulinic acid is not due to the presence of a carboxyl group, but is probably dependent on the presence of double linkings, for the acid can be removed from alkaline solutions by shaking with ether, and the bromine additive compound has neither an acid reaction nor a bitter taste; the acid is a derivative of an olefine terpene, for by melting it with potassium hydroxide an oil is obtained which, when distilled over phosphoric oxide, yields the *hydrocarbon* C_5H_8; it has an intense odour of leeks, similar to that of isoprene, a sp. gr. 0·8840 at 15° and n_D 1·4866 at 20°, but it does not show a constant boiling point, probably on account of polymerisation. Attempts to obtain aromatic compounds from the acid failed, but it is undoubtedly closely related to the ethereal hop oil which contains terpenes. The fact that pentosans constitute the main portion of the husks is of interest in connection with the presence of terpenes containing five carbon atoms. The acid forms an extremely unstable compound with sulphur dioxide.

α-Lupulinic acid (α-bitter acid), which is a constituent of α-resin, is a derivative of the terpene C_5H_8 and is also related to the β-acid and to hop oil. The products obtained by melting the α- and β-acids with potassium hydroxide are similar in odour and properties. By treating the α-acid with potassium hydroxide solution and sulphuric acid, an acid, $C_{15}H_{20}O_3$, melting at 84—85° is formed; the merest trace of this acid, when dissolved in chloroform and warmed with concentrated sulphuric acid, gives a violet coloration, but neither the α- nor the β-acid shows this reaction. The equivalent weights of the α- and β-acids are apparently nearly equal, hence the titration of the bitter principles in hops (Lintner, Abstr., 1899, ii, 264) involves no serious error. These acids are unsaturated compounds. E. W. W.

Bismarck-Brown. By Ernst Täuber and Franz Walder (*Ber.*, 1900, **33**, 2897—2899. Compare Abstr., 1898, i, 23 and 193).—Phenylenedisazo-*m*-phenylenediamine is the most important constituent of bismarck brown, and forms from 64—71 per cent. of the commercial product. Triaminoazobenzene is sometimes formed in appreciable quantities and nitroso-*m*-phenylenediamine and aziminobenzene have also been detected as impurities. From 15 to 20 per cent. of the crude base is insoluble in benzene, and the residue insoluble in acids may amount to 7 per cent. T. M. L.

Papaverinol. By Leo Stuchlik (*Monatsh.*, 1900, **21**, 813—830).—*Papaverinol*, $C_6H_3(OMe)_2 \cdot CH(OH) \cdot C_9NH_4(OMe)_2$, is obtained by the reduction of papaveraldine (Goldschmiedt, Abstr., 1886, 478) with zinc dust in glacial acetic acid solution; it crystallises in long, colourless, monoclinic needles [$a : b : c : = 0·671 : 1 : 0·3408$; $\alpha = 116°32'50''$], melts at 137°, forms a *hydrochloride* which melts indefinitely at 202°, yields a *platinichloride* which melts and decomposes at 168°, and has much the same physiological action as papaveraldine; the *picrate* crystallises in prismatic crystals, which melt and decompose at 171°; the *benzoyl* compound forms yellow needles, which melt at 126°; the p-*bromobenzoyl* compound melts at 194°, and the *phenylurethane* melts and decomposes at 180°. Papaverinol forms a *methiodide*, which crystallises in small, slender needles, and melts at 190°, and *additive products* with methyl chloride, ethyl bromide, and benzyl chloride which melt respectively at 182°, 172°, and 179°. R. H. P.

Stereoisomeric 2-Phenyl-6-Methylpiperidines. By Max Scholtz and Helmuth Müller (*Ber.*, 1900, **33**, 2842—2847).—The 2-phenyl-6-methylpiperidine previously described (Abstr., 1895, i, 563) is really a mixture of two isomeric bases which may be separated by conversion into their hydrochlorides and repeated treatment of these with boiling acetone; the insoluble 2-*phenyl*-6-*methylpiperidine hydrochloride* crystallises from water in glistening needles melting at 215—216°; the *base* obtained from it distils at 248—249°, the *platinichloride* melts at 208—209°, the *aurichloride* at 167—168°, the *hydriodide* crystallises in plates melting at 229—230°, and the *hydrobromide* also in plates melting at 180—181°.

The soluble *hydrochloride* yields a base, iso-2-*phenyl*-6-*methylpiperidine*, distilling at 254—258°; the *hydrobromide* does not crystallise readily, and melts at 182—183°; the *hydriodide* crystallises in colourless needles melting at 172—173°; the *platinichloride* in needles melting at 195—196°, and the *aurichloride* in plates melting at 120—121°.

Both bases are optically inactive, but are racemic compounds, as the former may be resolved by the aid of *d*-tartaric acid, and the *iso*-base by the aid of *d*-camphorsulphonic acid.

l : 2-*Phenyl*-6-*methylpiperidine* d-*tartrate*, $C_5NH_9PhMe,C_4H_6O_6,H_2O$, crystallises in hemihedral rhombic prisms [a : b : c = 0·87352 : 1 : 1·0886] and is less soluble than the *d*-tartrate of the *d*-base. The active *base* distils at 247—248°, and has a sp. gr. 0·9486 at 20° and $[\alpha]_D$ − 44·44°. The corresponding d-*base* has been isolated by the aid of *l*-tartaric acid and has a sp. gr. 0·9497 at 20° and $[\alpha]_D$ + 44·81°.

d-iso-2-*Phenyl*-6-*methylpiperidine* d-*camphorsulphonate* is less soluble than the salt of the *l*-base, it melts at 187—188°, and yields a d-*base* distilling at 254—256°, and having $[\alpha]_D$ + 0·92°. The same optically active base may be obtained directly by the addition of *d*-camphorsulphonic acid to the original mixture of the racemic bases, as the two isomeric camphorsulphonates of 2-phenyl-6-methylpiperidine do not crystallise. J. J. S.

New Reaction of Phosgene. By [Carl] Bernhard Kühn [and in part W. Spindler and P. von Gartzen] (*Ber.*, 1900, **33**, 2900—2904).—o-*Acetylaminobenzylpiperidine*, $NHAc\cdot C_6H_4\cdot CH_2\cdot C_5NH_{10}$, prepared by the action of acetic anhydride on the base (Lellmann and Pekrun, Abstr., 1891, 89) crystallises from light petroleum in small, white needles, melts at 76°, and dissolves in acids and organic solvents. Carbonyl chloride converts it into dipiperidylcarbamide (Wallach and Lehmann, Abstr., 1887, 385) and o-*acetylaminobenzyl chloride*, $NHAc\cdot C_6H_4\cdot CH_2Cl$, which crystallises from benzene and melts at 114°.

p-*Acetylaminobenzylpiperidine* crystallises from benzene and light petroleum in flakes and melts at 146°; the *acetate* crystallises from benzene in small rhombic crystals and melts at 114°; the *hydrochloride* melts at 218°. p-*Acetylaminobenzyl chloride*, produced by the action of carbonyl chloride, crystallises from benzene in flat, rhombic needles and melts at 155°.

m-*Acetylaminobenzylpiperidine* crystallises from a mixture of benzene and light petroleum in white, glistening needles and melts at 95°. m-*Acetylaminobenzyl chloride*, produced by the action of carbonyl chloride, crystallises from a mixture of benzene and light petroleum in needles and melts at 89°.

o-*Acetylaminophenylpiperidine*, $NHAc\cdot C_6H_4\cdot C_5NH_{10}$, is an oil boiling at 340°. Carbonyl chloride converts it into the chloroimide, which combines with aniline, forming *diphenylpiperidylethenylamidine*, $NHPh\cdot CMe\colon N\cdot C_6H_4\cdot C_5NH_{10}$; this crystallises from alcohol in brown needles, melts at 135°, and yields a crystalline *hydrochloride*, *picrate*, and *platinichloride*. T. M. L.

Organic Bases of Russian Petroleum. By Grigori V. Chlopin (*Ber.*, 1900, **33**, 2837—2841).—Caucasian petroleum contains about

0·005—0·006 per cent. of pyridine bases of the general formula $C_nH_{2n-15}N$. Six different fractions of the bases have been obtained by the aid of their platinichlorides, but whether the six fractions are homogeneous is questionable. The molecular weights of the different fractions lie between 104 and 308; the most complex fraction gives numbers which agree with those required for the formula $C_{22}H_{29}N$ for the *base* and $(C_{22}H_{29}N)_2,H_2PtCl_6$, for the *platinichloride*. The bases are poisonous in their action on fish, but not on white rats or cats. They do not possess disinfecting properties. J. J. S.

Condensation of Cyanoacetamide with Chloroform. By Giorgio Errera (*Ber.*, 1900, **33**, 2973—2976.)—From Guthzeit's researches (Abstr., 1899, i, 450), it is probable that the compounds previously described (Abstr., 1898, i, 298) as *α*-*γ*-dicyanoglutaconamide and *α*-carbonamido-*γ*-cyanoglutaconic acid are respectively the *ammonium* derivatives of 3 : 5-*dicyano*-2 : 6-*dihydroxypyridine*, $OH\cdot C_5NH(CN_2)\cdot O\cdot NH_4$, and of 5-*cyano*-2 : 6-*dihydroxypyridine*-3-*carboxylamide*, $OH\cdot C_5NH_5(CN)(CO\cdot NH_2)\cdot O\cdot NH_4$, or their ketonic tautomerides. The former compound may be crystallised from hydrochloric acid of sp. gr. 1·1, or boiled with aqueous sodium hydroxide (1 equivalent) without decomposition. Both compounds, when boiled with a large excess of alkali, are decomposed into a mixture of products. It appears that these substituted pyridines are very strongly acidic, being comparable with mineral acids.

The *monoamide* of 2 : 6-*dihydroxypyridine*-3 : 5-*dicarboxylic acid*, $CO_2H\cdot C_5NH(OH)_2\cdot CO\cdot NH_2$, obtained by boiling the above carbonamidopyridine with excess of alkali, crystallises in needles melting and decomposing at 213°. J. J. S.

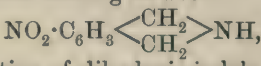
Mixed Methenyl Compounds. III. Action of Ethyl Ethoxymethylenacetoacetate on Cyanoacetamide. By Giorgio Errera (*Ber.*, 1900, **33**, 2969—2973. Compare Abstr., 1900, i, 33).—*Ethyl* 5-*cyano*-6-*hydroxy*-2-*picoline*-3-*carboxylate*, $OH\cdot C_5NHMe(CN)\cdot CO_2Et$, obtained in the form of its sodium derivative by the action of ethyl ethoxymethylenacetoacetate on the sodium derivative of cyanoacetamide, is best purified by conversion into its *potassium* derivative, $C_{10}H_9O_3N_2K$, which crystallises in colourless plates readily soluble in water, but only sparingly so in alcohol. The ester crystallises from alcohol in glistening plates, and when hydrolysed with concentrated sulphuric acid or aqueous potash yields 6-*hydroxy*-5-*carboxylamido*-2-*picoline*-3-*carboxylic acid*, $OH\cdot C_5NHMe(CO\cdot NH_2)\cdot CO_2H$, which separates from boiling water as a colourless, crystalline powder turning black at 300°. 6-*Hydroxy* 2-*picoline*-3 : 5-*dicarboxylic acid*, obtained by hydrolysing the amide with hydrochloric acid of sp. gr. 1·1 at 120°, crystallises in needles or plates containing $1H_2O$, which it readily loses at 100°, and then melts at 303°. 6-*Hydroxy*-2-*picoline*, $C_5NH_3Me\cdot OH$, is formed when the dibasic acid is heated with hydrochloric acid for a short time at 130°; it crystallises in glistening needles containing 4 or $5H_2O$, which it loses on exposure to air; the anhydrous base crystallises from benzene in thick crystals melting at 159° and readily soluble in alcohol. The *hydrochloride* contains water of crystallisation and melts at 80—85°, the *platinichloride* dissolves readily in ether, alcohol, or water.

3 : 5-*Dibromo-6-hydroxy-2-picoline*, $C_5NHBr_2Me \cdot OH$, obtained when the aqueous solution of the base is treated with bromine water, crystallises in needles melting at 238—239°.

Attempts to obtain ethyl malonomethylenacetoacetate have proved unsuccessful, as a mixture of ethyl methylenbisacetoacetate and ethyl dicarboxyglutaconate is formed. J. J. S.

Hydrindene. By JULIUS DÜNKELSBÜHLER (*Ber.*, 1900, **33**, 2895—2897).—*Nitrohydroxyhydrindene*, $C_9H_9O_3N$, prepared by the action of cold dilute nitric acid on hydrindene, crystallises from dilute alcohol, melts at 40°, and is volatile in steam. *Aminohydroxyhydrindene*, $C_9H_{11}ON$, forms colourless, glistening needles and melts and decomposes at 184°. Hydrindene has also been nitrated, but the nitro-derivatives are not described. T. M. L.

Dihydro*iso*indole (*o*-Xylylenimine). By KURT FRÄNKEL (*Ber.*, 1899, **33**, 2808—2818).—Phthalazonecarboxylic acid gives a sparingly soluble *ammonium* salt, $C_9H_{11}O_4N_3$, which crystallises in beautiful, white prisms melting at 237°. *Phthalazonecarboxylic chloride*, $C_9H_5O_2N_2Cl$, crystallises in dry benzene in white needles, sinters at 183°, and melts at 186°. *Ethyl phthalazonecarboxylate*, $C_9H_5O_3N_2Et$, forms beautiful, felted needles melting at 169°.

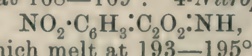
5-*Nitrodihydro*iso*indole*,  $NO_2 \cdot C_6H_3 < {CH_2 \atop CH_2} > NH$, made by adding fuming nitric acid to a solution of dihydro*iso*indole in sulphuric acid, is oily, but yields crystalline salts. It is converted into 4-nitrophthalic acid by oxidation with potassium dichromate and sulphuric acid. The *hydrochloride*, $C_8H_8O_2N_2,HCl$, forms white needles and melts above 250° ; the *sulphate* crystallises in needles and melts at 240—260° ; the *nitrate*, $C_8H_8N_2O_2,HNO_3$, forms quadratic prisms which melt and decompose at 158°. The *nitrosoamine*, $NO_2 \cdot C_8H_7N \cdot NO$, forms brownish-yellow prisms melting at 168—169°. 4-*Nitrophthalimide*,

$$NO_2 \cdot C_6H_3 \colon C_2O_2 \colon NH,$$

forms white needles which melt at 193—195°.

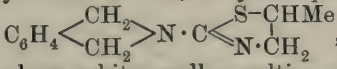
5-*Aminodihydro*iso*indole*, $NH_2 \cdot C_8NH_8$, is obtained by reducing the nitro-compound with stannous chloride ; its picrate, $C_8H_{10}N_2,C_6H_3O_7N_3$, forms yellow needles which melt at 203—204°.

*Benzoyldihydro*iso*indole*, C_8NH_8Bz, obtained from dihydro*iso*indole by the Baumann-Schotten reaction, is readily soluble in alcohol, benzene, and toluene, and separates from light petroleum in rose-coloured, quadratic tablets melting at 100°.

o-*Xylylenehydrazine*,  $C_6H_4 < {CH_2 \atop CH_2} > N \cdot NH_2$, prepared from the nitrosoamine by treatment with zinc dust and dilute acetic acid, is a brownish oil which absorbs carbon dioxide from the air and reduces warm Fehling's solution. The *hydrochloride*, $C_8H_8N \cdot NH_2,HCl$, forms white needles and melts at 190—194°. The *picrate*,

$$C_8H_8N \cdot NH_2,C_6H_3N_3O_7,\tfrac{1}{2}H_2O,$$

crystallises in long, yellow needles, melting at 96—97°. *Benzylidene-o-xylylenehydrazine*, $C_8H_8N_2 \colon CHPh$, crystallises from alcohol in pearly leaflets melting at 127—129°. o-*Hydroxybenzylidene*-o-*xylylenehydrazine*, $C_8H_8N_2:CH\cdot C_6H_4\cdot OH$, forms glistening leaflets melting at 165—166°.

*Dihydro*iso*indylphenylthiocarbamide*, $NHPh\cdot CS\cdot NC_8H_8$, crystallises from toluene in white leaflets melting at 226—227°. *Dihydro*iso*indylallylthiocarbamide* forms white needles melting at 138—139°; when heated with hydrochloric acid, it yields *propylenedihydro*iso*indyl-ψ-thiocarbamide*,  $C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>N\cdot C<\begin{matrix}S-CHMe\\ | \\N\cdot CH_2\end{matrix}$, which crystallises from ethyl acetate in long, white needles melting at 78—80°.

*Dimethyldihydro*iso*indylium iodide*, $C_8NH_8Me_2I$, prepared from dihydro*iso*indole and methyl iodide, forms shining leaflets and melts and darkens at 244—245°. The *platinichloride*, $(C_{10}H_{13}N)_2,H_2PtCl_6$, forms orange needles melting at 225°; the *picrate*, large needles melting at 145°; and the *aurichloride* yellow needles melting at 178°. The base absorbs carbon dioxide from the atmosphere and decomposes on distillation, yielding 2-*methyldihydro*iso*indole*, C_8NH_8Me. This boils at 205—215°, has an odour resembling that of train oil, and becomes coloured on exposure to the air; the *platinichloride*, $(C_9H_{11}N)_2,H_2PtCl_6$, forms brownish-yellow prisms melting at 200—201°.

2-γ-*Methoxypropyldihydro*iso*indole*, $C_8NH_8\cdot C_3H_6\cdot OMe$, from dihydro*iso*indole and methoxychloropropane, boils at 269—273°, and yields a solid *aurichloride*, $C_{12}H_{17}ON,HAuCl_4$.

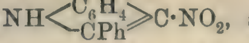
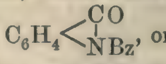
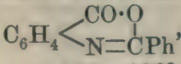
2-γ-*Phenoxypropyldihydro*iso*indole*, $C_8NH_8\cdot C_3H_6\cdot OPh$, crystallises from well-cooled light petroleum in nodular aggregates of white needles melting at 57—58°; the aurichloride, platinichloride, and picrate could not be obtained in a crystallised form.

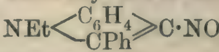
2-γ-*Bromopropyldihydro*iso*indole*, $C_8NH_8\cdot C_3H_6Br$, made by heating the foregoing phenoxy-compound with fuming hydrobromic acid at 100°, forms a yellow oil; the *hydrobromide*, $C_{11}H_{15}NBr_2$, forms white needles melting at 155—156°, and the *picrate*, $C_{17}H_{17}O_7N_4Br$, yellow needles and melts at 129—131°.

o-*Nitrobenzyldihydro*iso*indole*, $C_8NH_8\cdot CH_2\cdot C_6H_4\cdot NO_2$, crystallises from alcohol in yellow needles which melt at 80—81°; on reduction, it yields o-*aminobenzyldihydro*iso*indole*, $C_8NH_8\cdot CH_2\cdot C_6H_4\cdot NH_2$, which forms yellowish needles melting at 98—100°.

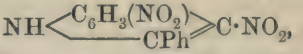
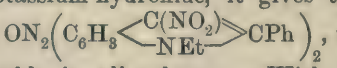
p-*Nitrobenzyldihydro*iso*indole* separates from alcohol in brownish-yellow needles and melts at 78—80°. A. L.

3-Nitroindoles. By ANGELO ANGELI and FRANCESCO ANGELICO (*Gazzetta*, 1900, **30**, ii, 268—283).—The position of the nitroso-group in the 3-nitrosoindoles is fixed by their behaviour on oxidation; thus, with alkaline permanganate, 3-nitroso-2-phenylindole yields benzoylanthranilic acid. On oxidation, the nitrosoindoles behave similarly to the nitrosophenols and yield the corresponding nitroindoles, which cannot be obtained by direct nitration of the indoles, as in this way polynitro-derivatives are always obtained; with nitrosoindoles containing an aliphatic radicle, the oxidation takes place best in alkaline solution, whilst if an aromatic substituent be present, acid and alkaline oxidation yield equally good results.

3-*Nitro-2-phenylindole*,  $NH<\begin{smallmatrix}C_6H_4\\CPh\end{smallmatrix}>C{\cdot}NO_2$, separates from acetic acid in lustrous, yellow crystals melting and decomposing at 238—239°. Oxidation of this compound and also of the corresponding nitroso-derivative yields benzoylanthranilic acid, which when heated with acetic anhydride, gives rise to an *anhydride*,  $C_6H_4<\begin{smallmatrix}CO\\|\\NBz\end{smallmatrix}$, or  $C_6H_4<\begin{smallmatrix}CO{\cdot}O\\|\\N{=}CPh\end{smallmatrix}$, separating from light petroleum in white crystals melting at 122—123°.

3-Nitro-2-phenyl-1-ethylindole,  $NEt<\begin{smallmatrix}C_6H_4\\CPh\end{smallmatrix}>C{\cdot}NO_2$, crystallises from alcohol in yellow needles melting at 175°.

3-*Nitro-2-methylindole*, $C_9H_8O_2N_2$, separates from dilute alcohol in shining, yellow scales with an azure surface colour melting at 237°.

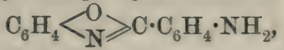
Dinitro-2-phenylindole,  $NH<\begin{smallmatrix}C_6H_3(NO_2)\\CPh\end{smallmatrix}>C{\cdot}NO_2$, obtained by mixing a hot acetic acid solution of the phenylindole with the calculated quantity of sodium nitrite and adding a large excess of concentrated nitric acid, crystallises from alcohol in yellow scales melting above 280°. *Dinitro-2-phenyl-1-ethylindole*, $C_{16}H_{13}O_4N_3$, separates from alcohol in sparkling, golden-yellow needles melting at 221°; on treatment with alcoholic potassium hydroxide, it gives the *azoxy*-compound of the constitution  $ON_2\left(C_6H_3<\begin{smallmatrix}C(NO_2)\\NEt\end{smallmatrix}>CPh\right)_2$, which does not melt at 285° and is insoluble in all solvents. With hydroxylamine hydrochloride in presence of sodium ethoxide, dinitro-2-phenyl-1-ethylindole yields an unstable oxime which is soluble in alkali solutions and has all the properties of a nitrohydroxylamine. T. H. P.

Iodo-derivatives of Quinoline, *iso*Quinoline, and 1-Methylquinoline. By ALBERT EDINGER and A. SCHUMACHER (*Ber.*, 1900, **33**, 2886—2892).—*Triiodoquinoline*, obtained by heating a mixture of quinoline, iodine, and fuming sulphuric acid containing 50 per cent. of trioxide for 5—6 hours at 100°, separates from benzene in stout, yellow crystals and from alcohol in nearly white needles; it melts at 189°, sublimes at 290°, and yields a yellow, crystalline *sulphate*, *hydrochloride*, and *platinichloride*, but fails to give a methiodide. Hot fuming nitric acid converts it into a *diiodonitroquinoline*, which crystallises from alcohol, or sublimes, in bright yellow needles and melts at 203°. The same compound is obtained, together with a crystalline *triiodonitroquinoline*, melting at 270°, on attempting to oxidise triiodoquinoline by heating for 2 hours at 210° with nitric acid of sp. gr. 1·12.

*Triiodo*iso*quinoline*, obtained in similar manner to triiodoquinoline, crystallises from alcohol in bright brown needles, melts at 253° and yields a yellow, crystalline *chloride*, *sulphate*, *nitrate*, and *platinichloride* (with $\frac{1}{2}H_2O$); the *methiodide* crystallises from water in bright yellow needles and decomposes at 280—285°. Fuming nitric acid at 100° converts triiodo*iso*quinoline into diiodonitro*iso*quinoline, which crystallises from glacial acetic acid in yellow needles and melts at 208°. *Diiodo*iso*quinoline* is a bye-product in the preparation of triiodo*iso*quinoline, especially when fuming sulphuric acid containing more than 50 per cent. of trioxide is employed; it crystallises from alcohol or xylene in white needles and melts at 151°, and yields a *platinichloride*, with $\frac{1}{2}H_2O$, which melts and decomposes at 300°.

When 1-methylquinoline is treated with iodine in the same way as quinoline and *iso*quinoline, it yields a *diiodo*-1-*methylquinoline* along with its *monosulphonic acid*; the former crystallises from xylene in white needles, melts at 171°, and yields a yellow, crystalline *hydrochloride, sulphate, nitrate,* and *platinichloride* (with $\frac{1}{2}H_2O$), whilst the latter crystallises from water, decomposes at 270°, and gives a crystalline *barium* salt with $1\frac{1}{2}H_2O$. The formation of the sulphonic acid is obviated by using fuming sulphuric acid containing more than 50 per cent. of trioxide. *Diiodonitro*-1-*methylquinoline* crystallises from alcohol and melts at 206°. W. A. D.

Benzazoles and Dyes derived from them. By Otto Kym (*Ber.*, 1900, **33**, 2847—2851. Compare Abstr., 1899, i, 674, 941; 1900, i, 190).—o-*Nitrophenyl*-p-*nitrobenzoate*, $NO_2\cdot C_6H_4\cdot CO_2\cdot C_6H_4\cdot NO_2$, crystallises from acetone in glistening plates melting at 139—140°, and when reduced yields 1-p-*aminophenylbenzoxazole*,



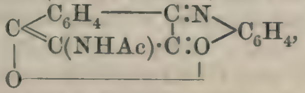
$$C_6H_4{<}\genfrac{}{}{0pt}{}{O}{N}{>}C\cdot C_6H_4\cdot NH_2,$$

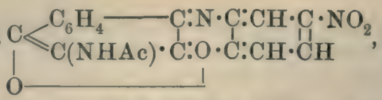
which crystallises in reddish-white needles melting at 173—174°.

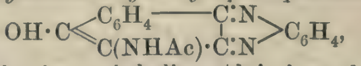
p-*Nitrobenzoyl*-o-*nitroaniline* is sparingly soluble in the usual solvents and melts at 219—220°. On reduction, it yields 2-p-*aminophenylbenziminazole*, $C_6H_4{<}\genfrac{}{}{0pt}{}{NH}{N}{>}C\cdot C_6H_4\cdot NH_2$, melting at 235—236° and yielding deep violet fluorescent solutions.

These two compounds and those previously described have been diazotised and combined with β-naphtholdisulphonic acid and with α-naphthol, and the dyes thus obtained tested on cotton. The position of the azo-group in the benzazoles appears to have little influence on the readiness with which the cotton takes up the dye, but those with the azo-group in the α-phenyl ring dye more intensely than their isomerides, and the dyes also exhibit a deeper bluish tone. When azo-groups are present in both rings, the tone is deepened enormously and the fabric is dyed much more readily. J. J. S.

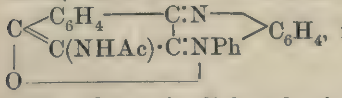
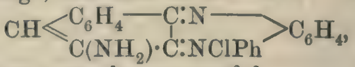
Syntheses of Oxazine and Azine Derivatives by Means of Acetaminonaphthalic Acid. By Friedrich Kehrmann and Gregoire Barche (*Ber.*, 1900, **33**, 3067—3074).—5-*Acetylaminophenonaphthoxazone*, $C{<}\begin{array}{l}C_6H_4\text{——}C{:}N\\ C(NHAc)\cdot C{:}O\end{array}{>}C_6H_4$ (with O joining C and C:O below), is formed when 5-acetylaminonaphthalic acid is heated with o-aminophenol and acetic acid, and crystallises in orange-yellow needles which decompose at about 310°. On hydrolysis, it yields 5-aminophenonaphthoxazone, which crystallises in slender, dark red needles melting at 211—212°, and is identical with the compound previously obtained by the nitration of phenonaphthoxazone and the reduction of the product, so that the constitution of this substance is thus established (Abstr., 1898, i, 45). 2-*Nitro*-5-*acetyl*-



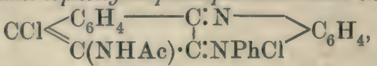
aminophenonaphthoxazone,  $\mathrm{C}\left<\begin{matrix}\mathrm{C_6H_4{-}C{:}N{\cdot}C{:}CH{\cdot}C{\cdot}NO_2}\\ \mathrm{C(NHAc){\cdot}C{:}O{\cdot}C{:}CH{\cdot}CH}\end{matrix}\right.$, is obtained from 4-nitro-*o*-acetylaminophenol, and crystallises in light, reddish-brown needles. The *base*, obtained by hydrolysis, crystallises in black, lustrous plates melting at 288°, and on reduction yields 2 : 5-*diaminophenonaphthoxazone*, $C_{16}H_{11}O_2N_3$, which crystallises in dark violet needles with a coppery lustre, and melts at 308°. The *diacetyl* derivative forms brick-red needles. 5-*Acetylamino*-6-*hydroxynaphthaphenazine*,



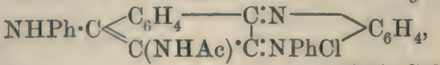
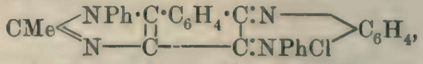
$$\mathrm{OH{\cdot}C}\left<\begin{matrix}\mathrm{C_6H_4{-}C{:}N}\\ \mathrm{C(NHAc){\cdot}C{:}N}\end{matrix}\right>\mathrm{C_6H_4},$$

formed when acetylaminonaphthalic acid is heated with *o*-phenylenediamine and acetic acid, melts at 257—258°. The *base* crystallises in small, dark violet needles melting at 225°. 5-*Acetylaminorosindone*,  $\mathrm{C}\left<\begin{matrix}\mathrm{C_6H_4{-}C{:}N}\\ \mathrm{C(NHAc){\cdot}C{:}NPh}\end{matrix}\right>\mathrm{C_6H_4}$, is obtained from acetylaminonaphthalic acid and *o*-aminodiphenylamine, and forms garnet-red needles melting at 249—250°. 5-*Aminorosindone* forms long, dark blue needles which resemble those of indigo, and melt at 215—216°. Attempts to prepare an *iso*rosinduline,  $\mathrm{CH}\left<\begin{matrix}\mathrm{C_6H_4{-}C{:}N}\\ \mathrm{C(NH_2){\cdot}C{:}NClPh}\end{matrix}\right>\mathrm{C_6H_4}$, from the acetyl derivative have hitherto proved unsuccessful.

6-*Chloro*-5-*acetylaminophenylnaphthaphenazonium chloride*,



$$\mathrm{CCl}\left<\begin{matrix}\mathrm{C_6H_4{-}C{:}N}\\ \mathrm{C(NHAc){\cdot}C{:}NPhCl}\end{matrix}\right>\mathrm{C_6H_4},$$

is prepared by the action of phosphorus pentachloride on acetylaminorosindone dissolved in phosphorus oxychloride, and is an orange-red, crystalline powder, the *platinichloride* being a bright red, crystalline precipitate. The *bromide* is precipitated by sodium bromide from the aqueous solution of the chloride, and closely resembles the latter. Aniline converts the chloride into 5-*acetylaminophenylrosinduline chloride*,  $\mathrm{NHPh{\cdot}C}\left<\begin{matrix}\mathrm{C_6H_4{-}C{:}N}\\ \mathrm{C(NHAc){\cdot}C{:}NPhCl}\end{matrix}\right>\mathrm{C_6H_4}$, which rapidly passes into an *iminazole* derivative,  $\mathrm{CMe}\left<\begin{matrix}\mathrm{NPh{\cdot}C{\cdot}C_6H_4{\cdot}C{:}N}\\ \mathrm{N{-}C{-}C{:}NPhCl}\end{matrix}\right>\mathrm{C_6H_4}$, crystallising in thick, dark brown, lustrous prisms; the *platinichloride* is a dark red, crystalline precipitate. A. H.

Action of Bromonitrobenzenes on *p*-Phenylenediamine. By Ernst Bandrowski (*Chem. Centr.*, 1900, ii, 852; from *Bull. Acad. Sci. Cracow*, 1900, 186—193).—*p*-Phenylenediamine does not act on *m*-bromonitrobenzene, but it slowly attacks *o*- and *p*-bromonitrobenzene, forming only nitrophenyl-*p*-phenylenediamine and not dinitrodiphenyl-*p*-phenylenediamine. p-*Nitrophenyl*-p-*phenylenediamine hydrochloride*, prepared by means of hydrochloric acid from the product obtained by heating a mixture of *p*-phenylenediamine, *p*-bromonitrobenzene, and sodium acetate in the mol. proportions 2 : 1 : 1 respectively (1 : 2 : 1 ?) with alcohol at 160—170°, separates from dilute hydrochloric acid in yellow crystals and loses hydrogen chloride on exposure to the air or more quickly by boiling with water.

p-*Nitrophenyl*-p-*phenylenediamine*, $NH_2{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2$, obtained from the hydrochloride by the action of ammonia, forms cherry-red, iridescent crystals, which have a metallic lustre, melts at 211—212°, and is slightly soluble in the ordinary solvents.

Acetyl-p-*nitrophenyl*-p-*phenylenediamine*, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}NHAc$, separates from alcohol in yellow crystals and melts at 22°. p-*Nitrophenylethyl*-p-*phenylenediamine*, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}NHEt$, prepared by warming *p*-nitrophenyl-*p*-phenylenediamine with ethyl iodide (1 mol.) in alcoholic solution, separates in dark red crystals and melts at 146—149°. By the action of benzaldehyde on *p*-nitrophenyl-*p*-phenylenediamine, p-*nitrophenylbenzylidene*-p-*phenylenediamine*, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}N{:}CHPh$ is obtained; it crystallises from alcohol in golden-yellow needles, melts at 219° and is sparingly soluble in alcohol. Di-*p*-diaminodiphenylamine, $NH(C_6H_4{\cdot}NH_2)_2$, is formed by the action of tin and hydrochloric acid on nitrophenyl-*p*-phenylenediamine.

Di-*p*-dibromoazobenzene, melting at 205°, and other products are also formed in the original reaction.

o-*Nitrophenyl*-p-*phenylenediamine*, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}NH_2$, prepared from *o*-bromonitrobenzene, crystallises in nearly black, pointed crystals which have a metallic lustre, melts at 105—106°, is rather easily soluble in hot alcohol and forms crystalline, orange-yellow salts. The *hydrochloride* crystallises in aggregates of needles. *Acetyl*-o-*nitrophenyl*-p-*phenylenediamine* crystallises from alcohol in dark red leaflets, and melts at 135—136°. o-*Nitrophenylbenzylidene*-p-*phenylenediamine* forms dark red crystals and melts at 98—99°.

o-*p*-Diaminodiphenylamine is formed by reducing nitrophenylphenylenediamine, but could not be isolated. E. W. W.

Stereochemistry of Nitrogen: Stereoisomeric Hydrazones of Ethyl Pyruvate. By L. J. Simon (*Compt. rend.*, 1900, 131, 682—684).—The action of phenylhydrazine on ethyl pyruvate in presence of alcohol yields two phenylhydrazones, identical in composition, molecular weight, and behaviour with reagents, but differing in melting point and solubility in organic solvents. One, which is formed in much the larger proportion, and is the less soluble, melts at 118—120°, whilst the other melts at 31—32°. C. H. B.

Action of Urethane on Aromatic Diamines. By C. Manuelli and V. Recchi (*Atti Real. Accad. Lincei*, 1900, [v], 9, ii, 269—272).—With ethylurethane, *o*-, *m*-, and *p*-phenylenediamines yield respectively *o*-, *m*-, and *p*-phenylenecarbamides. By treating the latter with an excess of phosphorus pentachloride and a few drops of oxychloride, the corresponding *chlorobenziminazoles*, $C_7H_5N_2Cl$, are obained; that obtained from *o*-phenylenecarbamide separates from aqueous alcohol as a white powder, which becomes brown on exposure to light, and melts at about 215°; the compound from *m*-phenylenecarbamide is white, but is turned brown by light, and does not melt definitely, but decomposes at about 200°; from *p*-phenylenecarbamide a compound was obtained which could not be purified. T. H. P.

3-Phenyl- and 3-Methyl-4:7-quinoquinoline-2-carboxylic Acids and their Derivatives. By CONRAD WILLGERODT and SIEGFRIED JABLONSKI (*Ber.*, 1900, **33**, 2918—2928. Compare *Chem. Zeit.*, 1900, **24**, 311, 437).—The authors have applied Doebner's method (Abstr., 1887, 504) to 6-aminoquinoline, and have thus obtained a number of substituted derivatives of 4:7-quinoquinoline [ψ-phenanthroline].

3-*Phenyl-ψ-phenanthroline*-2-*carboxylic acid*, $C_{12}N_2H_6Ph{\cdot}CO_2H$, obtained by the action of pyruvic acid and benzaldehyde on 6-aminoquinoline in alcoholic solution, is a yellowish, microcrystalline powder melting at 290°; it does not form additive compounds with alkyl haloids, but yields salts, both with acids and bases. The *sodium, potassium*, and *barium* salts crystallise in needles, whilst the *copper* and *silver* salts are amorphous and insoluble. The *platinichloride* is a brown, crystalline precipitate; the *nitrate*, $C_{19}H_{12}O_2N_2,2HNO_3$, crystallises in yellow plates, and the *hydrogen sulphate* forms pink cubes. The *methyl ester*, prepared from the silver salt, crystallises in colourless needles melting at 158°; the *ethyl ester* melts at 146°, and forms an *ethiodide*, melting at 225°. On nitration, the acid yields the 6-*nitro*-derivative, $NO_2{\cdot}C_{12}N_2H_5Ph{\cdot}CO_2H$, which melts at 310°, and on reduction is converted into the corresponding 6-*amino*-acid melting at 293°; the *platinichloride*, $C_{19}H_{13}O_2N_3,H_2PtCl_6$, is a crystalline powder.

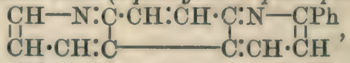
6-*Hydroxy*-3-*phenyl-ψ-phenanthroline*-2-*carboxylic acid*,

$$OH{\cdot}C_{12}N_2H_5Ph{\cdot}CO_2H,$$

obtained from the amino-acid by means of the diazo-reaction, is a crystalline powder, insoluble in indifferent solvents, but readily soluble in dilute alkalis. The 6-*chloro-acid*, $C_{19}H_{11}O_2N_2Cl$, is also prepared from the amino-acid and is a crystalline powder melting at 289°. The corresponding *bromo-acid* melts at 283°, and the *iodo-acid* at 272°. The bromo-acid is identical with that prepared from 8-bromo-6-aminoquinoline by the action of benzaldehyde and pyruvic acid, and hence both it and the amino- and nitro-compounds from which it has been obtained must have the constitution which has been assigned to them.

ψ-Phenanthroline-1:3-*dicarboxylic acid*, $C_{12}N_2H_6(CO_2H)_2$, obtained by the oxidation of phenyl-ψ-phenanthrolinecarboxylic acid with potassium permanganate, is a white powder melting at 248°; the *silver* salt is an amorphous white precipitate.

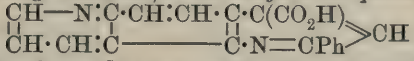
3-*Phenyl-ψ-phenanthroline* (3-*phenyl*-4:7-*quinoquinoline*),



$$\begin{array}{l} \mathrm{CH{-}N{:}C{\cdot}CH{:}CH{\cdot}C{:}N{-}CPh} \\ \mathrm{CH{\cdot}CH{:}C{-\!-\!-\!-}C{:}CH{\cdot}CH} \end{array},$$

is formed when sodium phenyl-ψ-phenanthrolinecarboxylate is distilled with soda-lime, and crystallises in white plates melting at 183°. The *platinichloride* is a grey, crystalline precipitate, and the *methiodide* crystallises in lustrous yellow needles melting at 242°. 6-*Nitro*-3-*phenyl-ψ-phenanthroline* is formed by the direct nitration of phenyl-ψ-phenanthroline and is also formed when sodium nitrophenyl-ψ-phenanthrolinecarboxylate is heated with soda-lime; it forms yellow crystals melting at 281° and on reduction yields the 6-*amino*-compound which crystallises in greenish plates melting at 222°. 6-*Hydroxy*-3-*phenyl-ψ-phenanthroline* is a yellowish-red, crystalline powder melting at 168°. 3-*Phenyl-ψ-phenanthroline*-6-*sulphonic acid*, $C_{12}N_2H_6Ph{\cdot}SO_3H$, is prepared by the sulphonation of phenyl-ψ-phenanthroline and forms a green, microcrystalline powder melting above 350°.

3-*Methyl-ψ-phenanthroline-2-carboxylic acid*, $C_{12}N_2H_6Me\cdot CO_2H$, prepared from aminoquinoline, pyruvic acid, and paraldehyde, is a deep red, microcrystalline powder which melts at 205°. The *sodium* salt crystallises in slender, light-yellow, hygroscopic needles, whilst the *copper* salt is amorphous. The *platinichloride*, $(C_{14}H_{10}O_2N_2)_2,H_2PtCl_6$, is formed when the acid is added to alcoholic platinic chloride, whilst another salt, $C_{14}H_{10}O_2N_2,H_2PtCl_6$, is produced by adding platinic chloride to a solution of the acid in hydrochloric acid. The *hydrogen sulphate* crystallises in light yellow, transparent needles. 3-*Methyl-ψ-phenanthroline*, $C_{12}N_2H_7Me$, crystallises in silky needles melting at 88°, and forms a crystalline *platinichloride*, a *methiodide* melting at 257°, and an *ethiodide* melting at 239°. A. H.

9-Phenyl-4 : 10-quinoquinoline-7-carboxylic Acid and 9-Methyl-4 : 10-quinoquinoline-7-carboxylic Acid. By Conrad Willgerodt and Erwin von Neander (*Ber.*, 1900, **33**, 2928—2935. Compare preceding abstract).—9-*Phenyl*-4 : 10-*quinoquinoline*-7-*carboxylic acid*,  $\begin{array}{l} CH{-}N{:}C\cdot CH{:}CH\cdot C\cdot C(CO_2H) \\ CH\cdot CH{:}C{-\!-\!-}C\cdot N{=}CPh \end{array}\!\!>\!CH$ [9-*phenylphenanthroline-7-carboxylic acid*] is prepared from 5-aminoquinoline, and forms yellow, microcrystalline needles melting at 353—355°; the *sodium*, *potassium*, and *ammonium* salts are soluble and crystalline, whilst the *copper* and *silver* salts are insoluble and amorphous. The *hydrochloride*, *nitrate*, and *hydrogen sulphate* are all crystalline salts, readily decomposed by water, and the *platinichloride* forms very small, reddish needles. The *methyl ester* melts at 158°, and forms a *methiodide* melting at 262°; the *ethyl ester* melts at 116°. 5-*Nitro-9-phenylphenanthroline-7-carboxylic acid*, $C_{19}H_{11}O_4N_3$, is a light yellow, microcrystalline powder melting at 285°; the corresponding *amino*-derivative melts at 302—303° and forms a *platinichloride*, $(C_{19}H_{13}O_2N_3)_2,H_2PtCl_6$. 5-*Chloro-9-phenylphenanthroline-7-carboxylic acid* melts at 278°, and the corresponding *bromo-acid* at 286—288°. The latter can also be prepared directly from 8-bromo-5-aminoquinoline. Phenylphenanthrolinecarboxylic acid is converted by sulphonation into a *sulphonic acid*, $C_{19}H_{11}O_2N_2(SO_3H)$, decomposing at 310°, the position of the sulphonic acid group in which has not yet been ascertained. 5-*Hydroxy-9-phenylphenanthroline-7-carboxylic acid* cannot be prepared from the amino-acid, but may be obtained by synthesis from 8-hydroxy-5-aminoquinoline; it is a yellow, microcrystalline powder melting at 293°. 9-*Phenylphenanthroline*, $C_{12}N_2H_7Ph$, is obtained from the carboxylic acid, and crystallises in compact white needles melting at 129°. The *platinichloride* is a reddish powder. 5-*Nitro-9-phenylphenanthroline* melts at 218°, and the corresponding *amino*-compound at 232°. This base forms two *platinichlorides*, $(C_{18}H_{13}N_3)_2,H_2PtCl_6$ and

$$(C_{18}H_{13}N_3)_2,3H_2PtCl_6.$$

9-Phenylphenanthroline readily yields a *sulphonic acid*, $C_{18}H_{11}N_2\cdot SO_3H$, which decomposes at 250°.

9-*Methylphenanthroline-7-carboxylic acid*, $C_{14}H_{10}O_2N_2$, melts at

309—310°, and yields a *sodium* salt which is more readily soluble in water than that of the corresponding phenyl derivative. A. H.

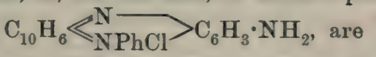
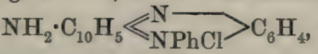
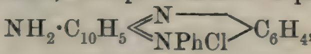
Thiopyrine. By August Michaelis and H. Bindewald (*Ber.*, 1900, 2873—2874).—5-Chloro-1-phenyl-3-methylpyrazole methiodide, which with alcoholic potash yields antipyrine (Abstr., 1899, i, 941), with alcoholic potassium hydrogen sulphide gives rise to *thioantipyrine* (*thiopyrine*), $C_{10}H_{12}N_2S$; this forms colourless, tabular crystals, melts at 166°, and yields a crystalline *hydrochloride*. The author considers the compound obtained by Silberstein (German Patent, 1899, 113384) from aniline, antipyrine, and phosphorus oxychloride to have the formula, $C_{10}H_{12}N_2\colon NPh$, analogous to thiopyrine, 5-chloro-1-phenyl-3-methylpyrazole methochloride being probably formed initially in this case. W. A. D.

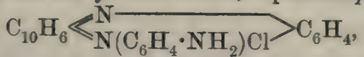
Preparation and Reactions of *iso*Phenosafranine. By Friedrich Kehrmann and Otto Kramer (*Ber.*, 1900, **33**, 3074—3081. Compare Abstr., 1900, i, 61).—Picryl chloride reacts with *o*-aminodiphenylamine to form picrylphenyl-*o*-phenylenediamine,

$$C_6H_2(NO_2)_3\cdot NH\cdot C_6H_4\cdot NHPh,$$

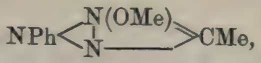
which crystallises in lustrous, garnet-red plates and at 120° loses nitrous acid, forming dinitrophenyldihydrophenazine. *iso*Phenosafranine is best prepared by reducing picrylphenyl-*o*-phenylenediamine with the calculated amount of stannous chloride in presence of alcohol and hydrochloric acid. Sulphuric acid converts *iso*phenosafranine into iso*safraninone*, $C_{18}H_{13}ON_3$, which crystallises in blackish-brown needles and melts and decomposes at 310—315°. The *chloride* crystallises in brown, lustrous needles, and the *nitrate* in blackish-brown needles.

The stannochloride of leuco*iso*safranine yields on treatment with acetic anhydride an *acetyl* derivative which rapidly oxidises, forming *monoacetyl*iso*phenosafranine*, the *chloride* of which, $C_{20}H_{17}ON_4Cl$, crystallises in violet-brown needles with a bronze lustre, whilst the *platinichloride* is a dark-red, microcrystalline precipitate. Acetic anhydride converts the chloride into the chloride of a *diacetyl* derivative, crystallising in needles with a bronze lustre. When a solution of the stannochloride of leuco*iso*phenosafranine is treated with sodium carbonate, ammonia, or aniline, the liquid becomes magenta-red on standing, owing to the production of *apo*safranine, ammonia being eliminated in considerable quantity. Since this substance can readily be converted into phenosafranine, this series of reactions provides a means of synthesising the latter important compound from picryl chloride and *o*-aminodiphenylamine. A. H.

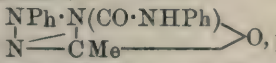
Relationship between the Constitution and Colour of Isomerides of Rosinduline. By Friedrich Kehrmann (*Chem. Centr.*, 1900, ii, 813—814; from *Arch. Sci. phys. nat. Genève*, [iv], **10**, 97—111. Compare Abstr., 1898, i, 154, 155; 1899, i, 238, 525; 1900, i, 60).—The alcoholic solutions of the amino-derivatives of phenylnaphthaphenazonium and phenyl*iso*naphthaphenazonium absorb much more light than those of the original compounds. The compounds which contain the amino-group in the para-position in regard to the quaternary nitrogen atom, as, for instance, 10-amino-7-phenylnaphthaphenazonium 7-chloride,  $C_{10}H_6{<}\genfrac{}{}{0pt}{}{N}{NPhCl}{>}C_6H_3\cdot NH_2$, are blue whilst those, on the other hand, in which the amino-group is in the para-position to the tertiary nitrogen atom, such as 5-amino-7-phenylnaphthaphenazonium 7-chloride,  $NH_2\cdot C_{10}H_5{<}\genfrac{}{}{0pt}{}{N}{NPhCl}{>}C_6H_4$, are red. The derivatives containing the amino-group in the other or non-quinonoid benzene ring of the naphthalene nucleus form bluish-green to greenish-yellow solutions in alcohol, except 3-amino-12-phenyl*iso*naphthaphenazonium 12-chloride,  $NH_2\cdot C_{10}H_5{<}\genfrac{}{}{0pt}{}{N}{NPhCl}{>}C_6H_4$, which gives a violet solution.

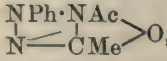
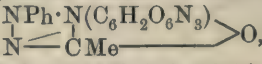
Isomerides of rosinduline in which the amino-group is contained in the benzene ring attached to the quaternary nitrogen atom (in position 7) have been prepared as follows. By condensing *o-p*-diaminodiphenylamine with 4-amino-β-naphthaquinone, a product containing an amino-group in the naphthalene ring in the para-position to the tertiary nitrogen atom is obtained, and by the action of acetic anhydride on this compound in the cold only the amino-group of the benzene ring is attacked. After removing the amino-group in the naphthalene ring by diazotisation, &c., and then hydrolysing the acetyl derivative, 7-p-*aminophenylnaphthaphenazonium* 7-*chloride*,  $C_{10}H_6{<}\genfrac{}{}{0pt}{}{N}{N(C_6H_4\cdot NH_2)Cl}{>}C_6H_4$, is obtained. This compound and the corresponding meta-derivative have practically the same colour as phenylnaphthaphenazonium itself, hence the introduction of the amino-group, in this case as in the similar case of the phenosafranines (*Ber.*, 1895, **27**, 3318), does not affect the colour. A complete table of the absorption spectra of the isomerides of rosinduline is given in the original paper. E. W. W.

Triazan Derivatives. By Hugo Voswinckel (*Ber.*, 1899, **33**, 2793—2798. Compare Abstr., 1899, i, 958).—The *silver* compound, $C_8H_8ON_3Ag$, of hydroxyphenylethenyl*cyclo*triazan is decomposed on crystallisation from aqueous ammonia, alcohol, or ether, but dissolves in benzene and can be precipitated from this solution by light petroleum.

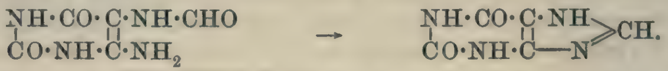
*Methoxyphenylethenyl*cyclo*triazan*,  $NPh{<}\genfrac{}{}{0pt}{}{N(OMe)}{N}{>}CMe$, obtained from the foregoing silver compound by means of methyl iodide, is a reddish oil which solidifies in a mixture of solid carbon dioxide and ether, melts below 0°, boils at 135° under 14 mm. pressure, is insoluble in water, but dissolves in alcohol, ether, or benzene, and with concentrated sulphuric acid gives the same intense coloration as the parent substance.

Phenylmethyl*cyclo*methylenetriazan is obtained by reducing the foregoing methyl ether with a cold alcoholic solution of stannous chloride. The *hydrogen oxalate*, $C_8H_{11}N,C_2O_4H_2$, forms a transparent, granular powder, and, after drying at 105°, melts at 200°.

*Carbanilphenylethylideneoxy*cyclo*triazan*,  $\begin{array}{l} NPh\cdot N(CO\cdot NHPh) \\ N{=}CMe \end{array}{>}O$, prepared from the hydroxytriazan and phenylcarbimide, crystallises in slender, orange needles melting at 127°, is insoluble in water and dilute alkali, but dissolves readily in benzene or hot absolute alcohol. From the latter medium, it separates on addition of water.

*Acetylphenylethylideneoxy*cyclo*triazan*,  $\begin{matrix}\text{NPh·NAc}\\ \text{N}=\text{CMe}\end{matrix}\!>\!\text{O}$, crystallises from dilute alcohol in beautiful, lustrous, golden needles melting at 103°, is soluble in alcohol, ether, or benzene, but insoluble in water, and is hydrolysed by cold, dilute alkalis or ammonia. *Picrylphenylethylideneoxy*cyclo*triazan*,  $\begin{matrix}\text{NPh·N(C}_6\text{H}_2\text{O}_6\text{N}_3\text{)}\\ \text{N}=\text{CMe}\end{matrix}\!>\!\text{O}$, forms small, shining, orange needles which explode at 140°, is insoluble in alcohol and light petroleum, but is readily soluble in benzene. A. L.

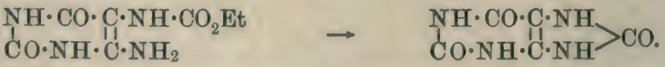
Synthesis of Uric Acid, Xanthine. Theobromine, Theophylline, and Caffeine from Cyanoacetic Acid. By WILHELM TRAUBE (*Ber.*, 1900, 33, 3035—3056. Compare Abstr., 1900, i, 416). —The formyl derivative of 4 : 5-diamino-2 : 6-dioxypyrimidine (*loc. cit.*) yields a sodium derivative, and when this is heated at 100—220° xanthine is formed :



$$\begin{matrix}\text{NH·CO·C·NH·CHO}\\ \text{CO·NH·C·NH}_2\end{matrix} \rightarrow \begin{matrix}\text{NH·CO·C·NH}\\ \text{CO·NH·C—N}\end{matrix}\!>\!\text{CH.}$$

The reaction of cyanoacetic acid with carbamide in the presence of phosphorus oxychloride is not satisfactory, however ; the yield can, indeed, be increased by adding pyridine, but in practice it is still better to convert cyanoacetic acid into xanthine by passing through guanine as an intermediate stage.

Just as 4 : 5-diamino-2 : 6-dioxypyrimidine will condense with formic acid, so it condenses with ethyl chloroformate in the presence of sodium hydroxide ; the *urethane* formed can be converted into a sodium derivative, and when this is heated at 150—190° uric acid is formed :

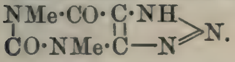


$$\begin{matrix}\text{NH·CO·C·NH·CO}_2\text{Et}\\ \text{CO·NH·C·NH}_2\end{matrix} \rightarrow \begin{matrix}\text{NH·CO·C·NH}\\ \text{CO·NH·C·NH}\end{matrix}\!>\!\text{CO.}$$

From carbamide both xanthine and uric acid can thus be prepared by means of cyanoacetic acid, &c. By a similar series of reactions methylcarbamide can be converted successively into *cyanoacetylmethylcarbamide*, 3-*methyl*-4-*amino*-2 : 6-*dioxypyrimidine*, the *isonitroso*-derivative of the latter, and 3-*methyl*-4 : 5-*diamino*-2 : 6-*dioxypyrimidine*. This forms on the one hand a *formyl* derivative, the sodium salt of which yields 4-methylxanthine (Fischer and Ach, Abstr., 1898, i, 700) ; on the other hand, it condenses with ethyl chloroformate to a *urethane*, and this, when heated to 230—240°, forms a 4-methyluric acid which may be either the δ (von Loeben, Abstr., 1898, i, 128) or the ζ acid (Fischer and Ach, Abstr., 1900, i, 63).

In like fashion, symmetrical dimethylcarbamide can be converted successively into 1 : 3-*dimethyl*-4-*amino*-2 : 6-*dioxypyrimidine* (the cyanoacetyldimethylcarbamide, which is presumably formed at first, undergoes an immediate conversion into the pyrimidine), its iso*nitroso*-

derivative, and 1 : 3-*dimethyl*-4 : 5-*diamino*-2 : 6-*dioxypyrimidine*. This yields a *formyl* derivative which melts at 252° and is converted into 4 : 6-dimethylxanthine (theophylline); it reacts with methyl iodide and alcoholic sodium ethoxide, forming 1 : 4 : 6-trimethylxanthine (caffeine); it condenses with ethyl chloroformate to a *urethane*, which melts at 206—207° and is converted into 4 : 6-dimethyluric acid (Fischer and Ach, Abstr., 1896, i, 12); and it reacts with sodium nitrite in hydrochloric acid solution forming an *azimide*,



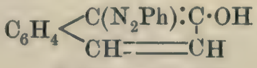
$$\begin{array}{l}\mathrm{NMe{\cdot}CO{\cdot}C{\cdot}NH} \\ \mathrm{CO{\cdot}NMe{\cdot}C{-}N}\end{array}\!\!>\!\mathrm{N}.$$

C. F. B.

Action of Methylene-Chlorohydrin on Aromatic Amines. By GIUSEPPE GRASSI-CRISTALDI and F. SCHIAVO-LENI (*Gazzetta*, 1900, **30**, ii, 112—122).—On mixing cold benzene solutions of aniline- and methylene-chlorohydrin, the hydrochloride of a reddish, oily *base*, $C_{28}H_{28}N_4$ (or $C_{14}H_{14}N_2$), is obtained. The base is slightly soluble in light petroleum, benzene, carbon disulphide, carbon tetrachloride, ether, or methyl or ethyl alcohol, and readily so in chloroform; it dissolves also in dilute sulphuric, hydrochloric, or acetic acid, yielding a red solution. The *hydrochloride* is white, but gradually becomes yellow and finally coral-red. The yellow *platinichloride*, $C_{28}H_{28}N_4,H_2PtCl_6$, loses 2HCl at 110°, giving the pale green *compound*, $C_{28}H_{28}N_4,PtCl_4$, whilst if the platinichloride is treated with boiling water until the latter has no longer an acid reaction, 4HCl are eliminated and a dark-green *product*, $C_{28}H_{26}N_4,PtCl_2$, remains.

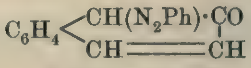
The homologous *base*, $C_{32}H_{36}N_4$ (or $C_{16}H_{18}N_2$), obtained from *o*-toluidine and methylene-chlorohydrin, is oily, and dissolves slightly in alcohol or ether and readily in chloroform; it also gives red solutions with dilute acids. The *platinichloride* is an amorphous, yellow powder which loses 2HCl and becomes pale green at 110°, whilst when treated with boiling water, 4HCl are evolved and a dark green *product*, $C_{32}H_{34}N_4,PtCl_2$, remains. T. H. P.

Unstable Isomerides of the Azo-derivatives of β-Naphthol. By MARIO BETTI [with GIOVANNI LEONCINI] (*Gazzetta*, 1900, **30**, ii, 164—177).—When prepared by the action of diazobenzene hydrochloride on a sodium hydroxide solution of β-naphthol and crystallised from alcohol, benzeneazo-β-naphthol is obtained in red needles with a green, metallic lustre melting at 133°; in benzene solution, it gives an intense violet coloration with ethereal ferric chloride, and hence appears to have an enolic structure. On boiling this compound with a 50 per cent. potassium hydroxide solution, it is converted into a black, crystalline mass which exhibits a contraction at 136°, melts at 180—185°, and when kept changes into microscopic, red needles having an indefinite melting point between 130° and 175°. The black crystals melting at 180—185° are completely soluble in alcohol, benzene, chloroform, acetone, acetic acid, or ethyl acetate, any of these solutions yielding, either by crystallisation, evaporation, or precipitation with water or light petroleum, red needles of an *isomeride* melting at 137°; the latter is also obtained, together with a black residue of the same composition melting at 185—187°, when the black crystals are recrystallised from light petroleum. The two modifications of benzenazo-β-naphthol thus obtained, melting at 133° and 137° respectively, yield the same nitro-derivative melting at 195°, but when brominated in acetic acid solution, the former gives a *heptabromo*-derivative, $C_{16}H_5ON_2Br_7$, separating from benzene in reddish-brown crystals with a metallic lustre and melting at 210—215° whilst the form melting at 137° gives rise to a *pentabromo*-compound, $C_{16}H_7ON_2Br_5$, crystallising from benzene as a lustrous red substance melting at about 250°. The following constitutions are ascribed to the two benzeneazo-β-naphthols:



$$C_6H_4\left<\begin{array}{l}C(N_2Ph){:}C\cdot OH\\ CH{=\!=\!=\!=}CH\end{array}\right.$$

Melting point 137°.



$$C_6H_4\left<\begin{array}{l}CH(N_2Ph)\cdot CO\\ CH{=\!=\!=\!=}CH\end{array}\right.$$

Melting point 183°.

o-Tolueneazo-β-naphthol, melting at 132°, when boiled with 50 per cent. aqueous potassium hydroxide, is converted into a black mass having a very marked green metallic lustre and melting at 115°. When kept, the colour of this substance rapidly changes to red, the melting point at the same time rising to 120—122°; by treatment with light petroleum, a black, insoluble mass melting at 120° is then separated from the red form which is found to be the original compound melting at 132°.

In a similar manner, *p*-tolueneazo-β-naphthol yields a brown modification which when heated in a melting point tube becomes lighter in colour and melts at the same temperature as the original compound.

T. H. P.

Condensation of Benzhydrols with *p*-Hydroxyazo-compounds and the Structure of the Latter. By Richard Möhlau and Ernst Kegel (*Ber.*, 1900, 33, 2858—2873).

—The *phenylhydrazone*, $NHPh\cdot N{:}C_{10}H_5O\cdot CH(C_6H_4\cdot NMe_2)_2$, of α-naphthaquinonetetramethyldiaminodiphenylmethane (Abstr., 1899, i, 912) is identical with the compound obtained from the condensation of benzeneazo-α-naphthol with "Michler's hydrol," $OH\cdot CH(C_6H_4\cdot NMe_2)_2$, in absolute alcohol; from the latter it separates in bright-red needles with a metallic lustre, melts at 200·5°, and is insoluble in aqueous alkalis. The *hydrochloride*, $C_{33}H_{32}ON_4,3HCl$, and the *picrate*, $C_{33}H_{32}ON_4,2C_6H_3O_7N_3$, form red needles, the latter melting and decomposing at 201°. The *acetyl* derivative crystallises in dark yellow, microscopic prisms, decomposes at 123°, and on reduction with zinc dust and acetic acid yields exclusively acetanilide and 1-*amino*-4-*naphthol*-2-*tetramethyldiaminodiphenylmethane*, $OH\cdot C_{10}H_5(NH_2)\cdot CH(C_6H_4\cdot NMe_2)_2$, which crystallises from ethyl acetate in colourless prisms, melts at 109—110°, and condenses with diazo-compounds in alkaline, but not in acid solutions; with warm hydrochloric acid it yields 1 : 4-*naphthaquinol*-2-*tetramethyldiaminodiphenylmethane*, $C_{10}H_5(OH)_2\cdot CH(C_6H_4\cdot NMe_2)_2$, which is readily oxidised by the air to the corresponding α-quinone, and yields a crystalline *hydrochloride*, $C_{27}H_{28}O_2N_2,2HCl$.

Benzhydrol does not interact with benzeneazo-α-naphthol in alcoholic solution, but when dissolved in glacial acetic acid they yield the *compound* $NHPh\cdot N{:}C_{10}H_5O\cdot CHPh_2$, which crystallises from benzene, on adding light petroleum, in microscopic, yellow plates, melts at 246—250°, and is insoluble in aqueous alkalis.

Diphenyldisazo-α-naphthol, $C_{12}H_8(\cdot N_2\cdot C_{10}H_6\cdot OH)_2$ or
$C_{12}H_8(NH\cdot N\colon C_{10}H_6\colon O)_2$,
obtained by combining α-naphthol with diazotised benzidine, crystallises from pyridine in prisms with a greenish lustre, softens at 200°, and melts at 209—210°; with Michler's hydrol, it yields the *compound*, $C_{12}H_8[NH\cdot N\colon C_{10}H_5O\cdot CH(C_6H_4\cdot NMe_2)_2]_2$, which crystallises from pyridine in bluish-violet, concentrically-grouped needles, sinters at 150° and melts at 164—165°; on reduction with zinc dust and warm hydrochloric acid, it yields benzidine and α-naphthaquinoltetramethyldiaminodiphenylmethane.

Dianisyldisazo-α-naphthol, $C_{34}H_{26}O_4N_4$, is a brownish, crystalline powder with a greenish lustre, which softens at 210°, melts at 218—219°, and dissolves in aqueous alkalis; with Michler's hydrol, it yields the *compound*, $C_{68}H_{66}O_4N_8$, which softens at 165°, melts at 180°, and could not be obtained crystalline.

Benzoquinonephenylhydrazonetetramethyldiaminodiphenylmethane,
$NHPh\cdot N\colon C_6H_3O\cdot CH(C_6H_4\cdot NMe_2)_2$,
from Michler's hydrol and *p*-hydroxyazobenzene dissolved in boiling absolute alcohol, crystallises from ethyl acetate in well-formed, yellow prisms and melts at 218°. No action occurs when *p*-methoxyazobenzene is boiled with Michler's hydrol for several days in absolute alcohol solution, and with benzeneazo-β-naphthol the same is true.

From the foregoing facts, the authors conclude that *p*-hydroxyazo-compounds in the free state are probably quinonehydrazones (compare McPherson, Abstr., 1900, 123; Hantszch and Farmer, *ibid.*, 122 Auwers, *ibid*, 418). W. A. D.

Tetrazones. By ANGELO ANGELI (*Atti Real. Accad. Lincei*, 1900, [v], **9**, ii, 180—183).—Nitrohydroxylaminic acid acts on piperidine with formation of products varying with the conditions of the reaction. Those which have been separated are: (1) the nitrosoamine, $C_5NH_{10}\cdot NO$; (2) a yellow oil with a nauseating odour recalling that of phosphorus and of its pentachloride; this is probably the oxyazo-compound, $ON_2(C_5NH_{10})_2$; (3) the tetrazone, $N_2(C_5NH_{10})_2$. T. H. P.

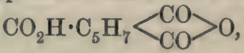
Proteids. By JOSEF HABERMANN and R. EHRENFELD (*Zeit. physiol. Chem.*, 1900, **30**, 453—472).—A critical and experimental examination of Schützenberger's results and theories concerning the decomposition products and constitution of proteids. W. D. H.

Nucleo-histon. By IVAR BANG (*Zeit. physiol. Chem.*, 1900, **30**, 508—519. By ALBRECHT KOSSEL (*ibid.*, 520—522).—According to the first paper, Lilienfeld's nucleo-histon is a nucleo-proteid, and it neither contains, nor yields, histon. The second paper is a criticism on the first; Lilienfeld's work is regarded as still trustworthy, the investigation published in the first paper having confused the issue whether there is such a thing as nucleo-histon with the question whether or no it is preformed in the cells. W. D. H.

Antipeptone. By MAX SIEGFRIED (*Ber.*, 1900, **33**, 2851—2858. Compare Abstr., 1895, i, 76; 1898, i, 611; 1899, i, 179).—Kuhne's method for the isolation of antipeptone does not give a pure product, since saturation with ammonium sulphate in neutral, alkaline, or acid solution does not precipitate the last traces of albumoses and since antipeptone itself when evaporated on the water-bath yields small amounts of albumoses. To completely precipitate the albumoses, it is necessary to use large quantities of sulphuric acid in addition to saturated ammonium sulphate, and then to precipitate with potassium iron alum ; the solution obtained by decomposing the iron precipitate can readily be freed from albumoses by stirring with saturated ammonium sulphate.

Two *acids*, $C_{10}H_{17}O_5N_3$ and $C_{11}H_{19}O_5N_3$ have been isolated from antipeptone and their *zinc* and *barium* salts prepared. Neither acid appears to be identical with carnic acid, for which the formula $C_{10}H_{15}O_5N_3$ has been previously suggested J. J. S.

Constitution of the Hæmatic Acids. By WILLIAM KÜSTER (*Ber.*, 1900, **33**, 3021—3025. Compare Abstr., 1899, i, 468).—The "anhydride of tribasic hæmatic acid," although it takes up 2 mols. of ammonia or aniline, appears to have the constitution



$$CO_2H\cdot C_5H_7{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}O,$$

for it yields no acetyl or benzoyl derivative, and a *trimethyl ester*, $C_5H_7(CO_2Me)_3$, boiling at 300° can be obtained from it, in addition to a trisilver salt. Among the saturated tribasic acids, $C_8H_{12}O_6$, obtained by reducing it with hydriodic acid, is one that resembles Auwer's ethyltricarballylic acid. By elimination of carbon dioxide, it yields the anhydride of a dibasic acid, $C_5H_8(CO_2H)_2$.

"Dibasic hæmatic acid" must then be regarded as the imide of the tribasic acid $CO_2H\cdot C_5H_7{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}NH$. In harmony with this view is the fact that its disilver derivative forms a methyl ester, when treated with methyl iodide, from which methylamine is obtained by hydrolysis. Moreover, it is formed from the anhydride of the tribasic acid by heating this with alcoholic ammonia at 110° ; at a somewhat higher temperature, carbon dioxide is eliminated, and a substance is obtained which has all the properties of an *imide* of the maleic series, $C_5H_8{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}NH$; it melts at 72—73°. This yields two barium salts when hydrolysed with barium hydroxide. One crystallises in plates ; acids react with this and form the *anhydride*, $C_5H_8{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}O$, which boils at 228—229°, and dissolves in alkalis ; the *silver*, *barium*, and *calcium* salts were prepared. The second of the two barium salts crystallises in needles ; the *acid* from which it is derived, $C_7H_{10}O_4$, is crystalline, and melts and decomposes at 175° ; it is, perhaps, a homologue of itaconic acid ; its *calcium* salt, $C_7H_8O_4Ca,H_2O$, crystallises in needles. C. F. B.

Protease of Aspergillus Niger. By G. MALFITANO (*Ann. Inst. Pasteur*, 1900, **14**, 420—448. Compare *ibid.*, 60).—The protease of *Aspergillus niger* resembles proteolytic diastases, and is very similar to papaine and the proteolytic diastase of malt. It acts on gelatin, on the nucleo-albumins, the globulins and albuminates, but not on egg-albumin.

As regards reaction, the most favourable is neutrality to methyl-orange, that is, the acidity of acid phosphates.

Protease differs from papaine only in being more sensitive to the injurious action of alkaline phosphates; it is very distinct from pancreatine, which is active in presence of alkaline phosphates.

N. H. J. M.

An Oxydase in Valerian. By P. Carles (*J. Pharm.*, 1900, [vi], **12**, 148—150).—The fact that valerian only acquires its odour on keeping, and that the freshly cut root gives an intensely blue coloration with tincture of guaiacum, suggests the presence of an oxydase in the plant; on bruising the root with a little water and adding alcohol, white flakes are precipitated which are extremely sensitive to the tests for oxydases. The oxydase is destroyed in the roots by heating them either alone or with water at 100°; like other oxydases, that of valerian appears to contain manganese, since this is present in quantity in the ash of the root. W. A. D.

Endotrypsin, an Enzyme from Yeast. By Martin Hahn and Ludwig Geret (*Zeit. Biol.*, 1900, **40**, 117—172).—The name *endotrypsin* is applied to an enzyme which is found in the liquid from crushed yeast cells, and which acts, not only on the proteids in the juice, but on other proteids as well. It is probably preceded in the cell-protoplasm by a zymogen, the transformation of which into enzyme occurs in accordance with the needs of the organism for intracellular katabolic processes. The enzyme is not dialysable; it is precipitated by most reagents that precipitate proteids, but does not give Millon's or the biuret reaction. The optimum temperature for its reaction is 40—45°; it continues acting at 37° for 15 days. It is destroyed at 60°. The enzyme appears to be a new type; it resembles pepsin in requiring the presence of an acid, and trypsin in the nature of its products. After digestion, leucine, tyrosine, and other amino-acids are found in abundance; proteoses are found in small quantity. Peptone as an intermediate product was not detected. W. D. H.

Expressed Yeast-Cell Plasma (Buchner's "Zymase"). By Allan Macfadyen, George Harris Morris, and Sidney Rowland (*Ber.*, 1900, **33**, 2764—2790; *Proc. Roy. Soc.*, 1900, **67**, 250—266). —A large number of experiments have been carried out by the authors on the extracts of various top-fermentation yeasts under conditions similar to those of Buchner's researches with bottom-fermentation yeasts. An improved method of treating the yeast has been devised which allows of quicker working than before. The yeast is well washed and then freed from water by enclosing it in a double thickness of hydraulic-press cloth and submitting it to a pressure of 70—100 atmospheres. The white powder thus obtained is mixed with sand and pounded in a specially designed apparatus, the temperature not being allowed to rise above 15°. Kieselguhr is then added and the extracted liquid separated by subjecting the mass to a pressure of 250—300 atmospheres. The resulting extract, which shows very wide variations in fermenting power probably differs less in composition from the ferment actually present in the living yeast cells than does that prepared by Buchner's method, in which water is mixed with the pounded yeast. The yield and also the activity of the extract is in general greatest from yeasts which have been removed from the fermenting vessels two or three days before treatment. The extract undergoes considerable fermentation on keeping, even at temperatures so low as to solidify it, and in nearly every case, the evolution of carbon dioxide was greater than when sugar was present. The action on sugar is increased by rise of temperature and of the various sugars sucrose gives the greatest volume of gas. Dilution of the extract with an equal volume of water diminishes its activity, whilst if two volumes of water be added the evolution of gas is considerably decreased. Marked diminution in activity accompanied by a decrease in the specific gravity is also produced by passing the extract through a Chamberland or Berkefeld filter. In the case of very active extracts, the ratio of the amounts of alcohol and carbon dioxide formed by their action on sugar is approximately the same as in ordinary fermentation by yeast, but with those less active there seems to be no definite relation existing between the proportions of these products. At the same time, the quantity of sugar destroyed is far greater than corresponds with the amounts of alcohol and carbon dioxide formed during fermentation.

To explain their results, which are not in accord with Buchner's enzyme theory of the fermenting action of yeast extract, the authors suppose that the fermentation of sugar solutions by yeast takes place in two stages (1) incorporation of the sugar molecule with the living yeast (anabolism); (2) decomposition of the complicated material thus formed into simpler products, generally carbon dioxide and alcohol (katabolism). These assumptions made, the auto-fermentation of the yeast extract is explained as due to the presence in it of a protoplasm-sugar compound, which undergoes gradual decomposition with formation of carbon dioxide and alcohol; in the case of an active extract, this decomposition proceeds nearly to completion, whilst with one less powerful, the activity of the protoplasmic constituent causing the fermentation ceases, while an excess of sugar still remains in the solution in combination with it. T. H. P.

Organic Chemistry.

Analogies between Oxygen, Nitrogen, and Carbon in similar Linkings. By Emil Erlenmeyer, jun. (*J. pr. Chem.*, 1900, [ii], **62**, 145—165).—A paper which summarises the results of introducing different atomic groupings into analogous compounds, but does not lend itself to abstraction. R. H. P.

Action of Bromine on 1 : 1-Dimethyltrimethylene. By Gabriel Gustavson (*J. pr. Chem.*, 1900, [ii], **62**, 270—272).—The bromine compound previously described (Gustavson and Popper, Abstr., 1899, i, 263), and obtained by the action of bromine on 1 : 1-dimethyltrimethylene (1 : 1-dimethyl*cyclo*propane), is $\beta\gamma$-dibromo*iso*butane, $CMe_2Br\cdot CHMeBr$. R. H. P.

Derivatives of *cyclo*Pentadiene. By Fritz Noeldechen (*Ber.*, 1900, **33**, 3348—3354).—The chloro*cyclo*pentene obtained by the addition of hydrogen chloride to Kraemer and Spilker's *cyclo*pentadiene (Abstr., 1896, i, 289) interacts with aniline below 10° to form *anilino*cyclo*pentene*, $C_5H_7\cdot NHPh$, a colourless oil boiling at 152—153° under 25 mm., and at 260° under the ordinary pressure; the *hydrochloride* crystallises from absolute alcohol in short prisms, and melts and decomposes at 140—142°; the *platinichloride* (with $1\frac{1}{2}H_2O$) decomposes at 140°; the *picrate* melts and decomposes at 154—155°, the sparingly soluble *sulphate* at 197°, and the *oxalate* at 122°. The *acetyl* derivative, $C_5H_7\cdot NAcPh$, crystallises from water in long needles, and melts at 128°; the *benzoyl* derivative separates in transparent, hexagonal prisms from light petroleum and melts at 76—77°.

cyclo*Pentenyldiphenylcarbamide*, $NHPh\cdot CO\cdot NPh\cdot C_5H_7$, obtained by the action of phenylcarbimide on the base at the ordinary temperature, separates from absolute alcohol in small leaflets and melts at 112°; the analogous *thiocarbamide* crystallises from absolute alcohol in lustrous, colourless needles and melts at 130°.

Anilino*cyclo*pentene interacts with nitrous acid to form a reddish-yellow, oily *nitrosoamine*, which shows Liebermann's reaction, and is reduced by zinc dust and acetic acid to cyclo*pentenylphenylhydrazine*, $NH_2\cdot NPh\cdot C_5H_7$, the *hydrochloride* of which forms silvery scales and melts and decomposes at 215—217°.

On heating anilino*cyclo*pentene with hydriodic acid, or with concentrated hydrochloric acid for 2 hours at 200°, aniline is formed, together with a red, amorphous, insoluble substance. On attempting to reduce the base with sodium and amyl alcohol, an isomeric *anilino*cyclo*pentene* is formed, instead of the expected anilino*cyclo*pentane; its *hydrochloride* is more sparingly soluble than that of the original base, and forms long, white needles melting and decomposing at 168°; the *platinichloride* (with $2H_2O$) decomposes at 135°.

*Piperidyl*cyclo*pentene*, $C_5H_{10}N\cdot C_5H_7$, from chloro*cyclo*pentene and piperidine at $-5°$, boils at 94—96° under 23 mm., and at 206—207°

under the ordinary pressure; it absorbs carbon dioxide from the air, yields a crystalline *methiodide*, and a hygroscopic *hydrochloride* and *sulphate*, the former decomposing at 190°. W. A. D.

Abnormal Behaviour of Polyhaloid Compounds with Alcoholic Potash. By Iwan L. Kondakoff (*J. pr. Chem.*, 1900, [ii], **62**, 166—188. Compare Abstr., 1899, i, 556).—The previous work (*loc. cit.*) has been repeated, and it is now shown that the action of alcoholic potash on βγ-dimethyl-β-butylene dibromide produces di*iso*propenyl, βγ-dimethyl-β-butylene, and an unsaturated *ether*, which boils at 136—146°, and, when treated with dilute sulphuric acid, gives pinacone, pinacolin, and an aldehyde. βγ-Dimethyl-β-butylene dichloride, when treated with alcoholic potash, yields di*iso*propenyl and the ether boiling at 136—146°.

Di*iso*propenyl forms two *dibromides*, the one is an oil, and the other crystallises in colourless needles, which have an irritating odour and melt at 47°, both yield the same *tetrabromide* melting at 137°. The crystalline dibromide, when oxidised, yields two glycols, of which one has the composition $C_6H_{12}O_2Br_2$, crystallises in prisms, and melts at 94°; the other, obtained in very small quantity, melts at 160°.

The paper contains a discussion of the constitution of bromides formed by unsaturated hydrocarbons from the point of view of Thiele's theory of "partial" valencies (Abstr., 1899, i, 554).

R. H. P.

Diethyl Peroxide. By Adolf von Baeyer and Victor Villiger (*Ber.*, 1900, **33**, 3387—3393).—Diethyl sulphate was shaken with hydrogen peroxide of 12 per cent. strength (by weight), 50 per cent. aqueous potassium hydroxide being added little by little; the temperature was not allowed to rise above 20°, and the operation was continued (for some 11 hours) until the presence of hydrogen peroxide could be detected no longer. The product was then made acid with sulphuric acid and fractionated; the fraction coming over at 55—75° consisted mainly of diethyl peroxide, that distilling at 75—100° probably contained some ethyl hydrogen peroxide. *Diethyl peroxide*, O_2Et_2, boils at 65°, and has a sp. gr. 0·8273 at 15°/4°; it is strikingly inert in its reactions, almost resembling an ether; permanganate, chromic acid, and sodium amalgam do not affect it, and it oxidises alkaline pyrogallol and potassium iodide but slowly; it is, however, reduced quantitatively to ethyl alcohol by zinc in the presence of acetic and dilute sulphuric or hydrochloric acid; the "active" oxygen in it may be determined in this way by taking a weighed quantity of zinc and measuring the deficit in the hydrogen evolved as compared with that equivalent to the amount of zinc taken. The inflammability of the vapour is most striking; it inflames in air at 250°, or 50° below the kindling temperature of carbon disulphide vapour, and when a hot copper wire is brought near it in an atmosphere of carbon dioxide, the liquid disappears rapidly, without any noise, without any flash, and without boiling. As a result of this internal combustion, formaldehyde, carbon monoxide, and ethane are formed. A mixture of the vapour with air or oxygen explodes more violently than a mixture of hydrogen with air or oxygen. On the other hand, the liquid could not be made to explode by hammering, or by the use of mercury fulminate.

The ready reduction of diethyl peroxide to ethyl alcohol is regarded as strong evidence in favour of the formula HO·OH, rather than $O\colon OH_2$, for hydrogen peroxide. C. F. B.

Optically Active Forms of α-Bromopropionic Acid. By LUDWIG RAMBERG (*Ber.*, 1900, **33**, 3354—3356).—On adding cinchonine gradually to an aqueous solution of α-bromopropionic acid, thick prisms or plates of the *salt*, $C_{19}H_{22}ON_2,2(C_3H_5O_2Br)$, of the l-*acid* separate; the pure acid appears to have $[\alpha]_D$ $-7·55°$ at 24°, the d-*acid*, isolated from the mother liquors of the foregoing salt, having $[\alpha]_D$ $+7·44°$. These values, however, are to be more accurately determined. W. A. D.

δε-Hexenoic Acid. By FRITZ FICHTER and WERNER LANGGUTH (*Annalen*, 1900, **313**, 371—381. Compare Wallach, Abstr., 1900, i, 589).—The paper contains experimental details relating to the preparation of δε-hexenoic acid (Abstr., 1897, i, 590), and of γδ-hexenoic acid (Abstr., 1897, i, 14). M. O. F.

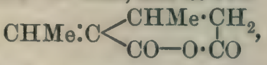
Action of Water on Heptylamine Soaps. By FRIEDRICH KRAFFT and R. FUNCKE (*Ber.*, 1900, **33**, 3210—3212).—When heptylamine oleate (m. p. 14°), elaidate (m. p. 45°), erucate (m. p. 21·5°), or brassate (m. p. 44·5°) is brought into contact with water at a temperature above the melting point, globular or thread-like bodies are produced, which grow in size when surrounded with water, but collapse in contact with a strong salt solution, the surface of the globules acting as a semipermeable membrane. By cooling below the melting point, the globules disappear and crystals are again formed; within certain limits of temperature, globules and crystals may both be observed. T. M. L.

Transformation of Maleic Acid into Fumaric Acid. By JULIUS SCHMIDT (*Ber.*, 1900, **33**, 3241—3243. Compare Wislicenus, *Verhand. K. Ges. Wiss. Leipzig*, 1895, 489).—Maleic acid, dissolved in dry ether, is not affected by the nitrous fumes evolved from a mixture of arsenious oxide and nitric acid; an aqueous solution, cooled below 10°, when similarly treated, yields a mixture of unaltered substance and fumaric acid, whilst at the temperature of the water-bath 70 per cent. of the maleic acid is transformed. Fumaric acid is not produced when an aqueous solution of its *cis*-isomeride is heated on the water-bath, and no alteration results from the addition of nitric acid free from nitrous acid (compare Edmed, Proc., 1899, **15**, 190).

G. T. M.

Dicrotonic Acid. By HANS VON PECHMANN (*Ber.*, 1900, **33**, 3323—3341).—*Dimethyl dicrotonate* (dimethyl β-methyl-α-ethylideneglutarate), formed by the action of sodium methiodide on dimethyl crotonate, is a colourless oil boiling at 120° under 15 mm. and at 130° under 20 mm. pressure; it is also formed when dicrotonic acid is treated with diazomethane. *Diethyl dicrotonate* is prepared from diethyl crotonate, and boils at 137·5° under 18 mm. pressure. *Dicrotonic acid*, $CHMe\colon C(CO_2H)·CHMe·CH_2·CO_2H$, prepared from the ester by hydrolysis, crystallises in white, compact needles melting at 129°, and boils

f 2

at 210° under 21 mm. pressure, partial decomposition into water and anhydride taking place. The acid is dibasic to soda, and has a conductivity *K* 0 00281. The difference of equivalent conductivity of the sodium salt at dilutions of 32 litres and 1024 litres is 11·9, an abnormally low value for a dibasic acid. The *barium* salt crystallises with $1H_2O$ in lustrous scales; no acid salts could be obtained. *Monoethyl dicrotonate*, $CHMe\dot{:}C(CO_2H){\cdot}CHMe{\cdot}CH_2{\cdot}CO_2Et$, is obtained by the action of alcoholic sodium ethoxide on dicrotonic anhydride, and is an oil boiling at 174° under 16 mm., at 186° under 34 mm., and at 192° under 44 mm. pressure. *Dicrotonic anhydride*,  $CHMe\dot{:}C<\begin{matrix}CHMe{\cdot}CH_2\\ CO{-}O{\cdot}CO\end{matrix}$, formed when the acid is distilled under atmospheric pressure or treated with acetyl chloride, crystallises in white needles melting at 38·—39° and boiling at about 300°.

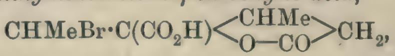
The constitution of the acid is shown by the fact that on oxidation with potassium permanganate it yields acetaldehyde and methylsuccinic acid.

β-Methyl-α-ethylideneglutaranilic acid,

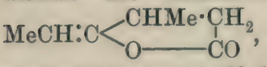
$$CHMe\dot{:}C(CO_2H){\cdot}CHMe{\cdot}CH_2{\cdot}CO{\cdot}NHPh,$$

is obtained by the action of aniline on the anhydride, and crystallises in lustrous prisms melting at 178—179°.

Dicrotonic acid readily combines with bromine to form an unstable *dibromide*, which loses hydrogen bromide when heated with water and forms *δ-bromo-β-methylhexolactone-γ-carboxylic acid*,



$$CHMeBr{\cdot}C(CO_2H)<\begin{matrix}CHMe\\ O{-}CO\end{matrix}>CH_2,$$

which crystallises in colourless prisms melting at 140°. When its solution in sodium carbonate is boiled, hydrogen bromide and carbon dioxide are eliminated with formation of *β-methylhexenolactone*,  $MeCH\dot{:}C<\begin{matrix}CHMe{\cdot}CH_2\\ O{-\!-\!-}CO\end{matrix}$, which is a colourless oil boiling at 247°. The corresponding acid, *βδ-dimethyllævulic acid*,

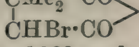
$$CH_2Me{\cdot}CO{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H,$$

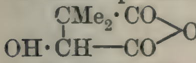
is a thick oil boiling at 153—154° under 20—21 mm. pressure. The *phenylhydrazone* is a thick oil, whilst the *semicarbazone*, $C_7H_{12}O_2\dot{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$, is a characteristic, white, crystalline powder melting at 152°. When heated, it yields a pyridazinone, probably a homologue of the 3-methylpyridazinone, which is formed in a similar manner from the semicarbazone of lævulic acid. βδ-Dimethyllævulic acid can be prepared synthetically from acetonedicarboxylic acid, and its formation in this way affords further confirmation of the constitution of dicrotonic acid. Ethyl dimethylacetonedicarboxylate reacts with ethyl bromoacetate to form *triethyl αα₁-dimethylacetonedicarboxyacetate*, $CO_2Et{\cdot}CHMe{\cdot}CO{\cdot}CMe(CO_2Et){\cdot}CH_2{\cdot}CO_2Et$, which boils at 191·5° under 16 mm. pressure. *β-Methyl-γ-bromoethylglutaric acid*,

$$CHBrMe{\cdot}CH(CO_2H){\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H,$$

is formed by the combination of hydrogen bromide with dicrotonic acid and crystallises in aggregates of needles; the acid readily loses bromine, and could not be obtained quite pure. When distilled, it forms crotonic acid together with a smaller amount of *β-methyl-γδ-hex-*

enoic acid, $CHMe\colon CH\cdot CHMe\cdot CH_2\cdot CO_2H$, which is also formed when the acid is heated with water. It is a colourless liquid with a rancid smell, and boils at 209—210°. With bromine, it forms *γδ-dibromo-β-methylhexoic acid*, $CHBrMe\cdot CHBr\cdot CHMe\cdot CH_2\cdot CO_2H$, which crystallises in rhombic tablets and melts at 135—136°. *β-Methyl-α-ethylglutaric acid*, $CO_2H\cdot CHEt\cdot CHMe\cdot CH_2\cdot CO_2H$, is formed by the reduction of β-methyl-γ-bromoethylglutaric acid and crystallises in colourless prisms melting at 100—101°; $K = 0{\cdot}0067$. A. H.

The β-Lactone of *as*-Dimethylmalic Acid. By FRITZ FICHTER and SYLVAIN HIRSCH (*Ber.*, 1900, **33**, 3270—3276).—Bromo-*as*-dimethylsuccinic acid, which could not be obtained pure by von Baeyer and Villiger (Abstr., 1897, i, 597), yields on distillation the pure *anhydride*,  $\begin{array}{l} CMe_2{-}CO \\ | \\ CHBr\cdot CO \end{array}\!\!>O$, which forms stout needles, melts at 45°, and boils at 121—123° under 13 mm. pressure. On evaporating its aqueous solution in a vacuum, the pure acid, $C_6H_9O_4Br$, is obtained as a hard, crystalline crust melting at 153°; if the anhydride is dissolved in benzene containing water, slender needles of the acid with $\frac{1}{2}C_6H_6$ separate, which melt at 133°, and effloresce in the air, the acid thus obtained melting at 143°.

The β-lactone of *as*-dimethylmalic acid distils at 145—150° under 13 mm. pressure, being converted into the isomeric *anhydride*,  $\begin{array}{l} \quad\;\; CMe_2\cdot CO \\ \quad\;\; | \\ OH\cdot CH{-}{-}CO \end{array}\!\!>O$, a colourless oil which is also formed on distilling *as*-dimethylmalic acid under the same conditions, although decomposition occurs at atmospheric pressure. Since the anhydride readily absorbs water from the air to form dimethylmalic acid, it differs essentially from the isomeric lactone which crystallises from water unchanged. W. A. D.

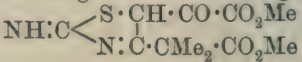
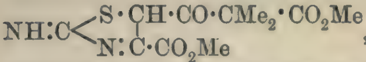
Oxalyldialkylacetoacetic Esters. By MAX CONRAD (*Ber.*, 1900, **33**, 3432—3438).—*Methyl oxalyldimethylacetoacetate*,

$$CO_2Me\cdot CO\cdot CH_2\cdot CO\cdot CMe_2\cdot CO_2Me,$$

prepared by the action of sodium on an ethereal solution of methyl oxalate and methyl dimethylacetoacetate and purified by converting into the copper compound, is a pale yellow oil which has a sp. gr. 1·193 at 17°/15°, boils and partially decomposes at 270—278°, has a distinct acid reaction, mixes readily with ether, alcohol, or benzene, and gives a cherry-red coloration with alcoholic ferric chloride. The *calcium* derivative, $Ca(C_{10}H_{13}O_6)_2$, dissolves in ether, softens at 115°, and melts at 125°; the *cobalt* derivative, $Co(C_{10}H_{13}O_6)_2$, melts at 98—100°; the *copper* derivative, $Cu(C_{10}H_{13}O_6)_2$, melts at 128—130°; the compound with *ammonia*, $C_{10}H_{17}O_6N$, forms minute, white needles, and melts at 110°. *Methyl anilino-oxalyldimethylacetoacetate*, $CO_2Me\cdot C(NHPh)\colon CH\cdot CO\cdot CMe_2\cdot CO_2Me$, or

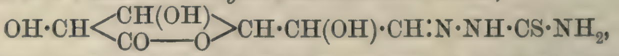
$$CO_2Me\cdot CO\cdot CH\colon C(NHPh)\cdot CMe_2\cdot CO_2Me,$$

crystallises from methyl alcohol in large, well-formed, sulphur-yellow prisms and melts at 81°; the *monoxime*, $C_{10}H_{15}O_6N$, crystallises from hot water and melts at 91°. *Oxalyldimethylacetoacetic acid* forms colourless crystals, melts at 180° with evolution of carbon dioxide, and also loses carbon dioxide in aqueous solution at 70—80°, giving an *iso*butyrylpyruvic acid.

Methyl bromo-oxalyldimethylacetoacetate is a yellow oil; it forms a *copper* derivative, $Cu(C_{10}H_{12}BrO_6)_2$, crystallising from ether in green needles. The *thiazyl* derivative,  $NH{:}C\left\langle\begin{matrix}S\cdot CH\cdot CO\cdot CO_2Me\\ N{:}C\cdot CMe_2\cdot CO_2Me\end{matrix}\right.$ or  $NH{:}C\left\langle\begin{matrix}S\cdot CH\cdot CO\cdot CMe_2\cdot CO_2Me\\ N{:}C\cdot CO_2Me\end{matrix}\right.$, prepared by the action of thiocarbamide on the bromo-ester, crystallises from hot water in white needles and melts at 138°. By the action of potassium acetate on the bromo-ester in methyl alcoholic solution, methyl oxalate and the acetate of methyl hydroxydimethylacetoacetate are produced as decomposition products of methyl acetoxyoxalyldimethylacetoacetate.

Ethyl oxalyldiethylacetoacetate, $CO_2Et\cdot CO\cdot CH_2\cdot CO\cdot CEt_2\cdot CO_2Et$, is a colourless oil which forms a copper derivative and gives a red coloration with alcoholic ferric chloride. By distillation, it gives *ethyl aa-diethylacetonedicarboxylate*, $CO_2Et\cdot CH_2\cdot CO\cdot CEt_2\cdot CO_2Et$, boiling at 275—285°. T. M. L.

Glycuronic Acid. I. By CARL NEUBERG (*Ber.*, 1900, **33**, 3315—3323).—Several of the compounds described by the author have been previously described by Giemsa (this vol., i, 11). Glycuronolactane (glycurone) is best obtained by boiling euxanthic acid with dilute sulphuric acid. *Glycuroneamylmercaptal* was only obtained in the form of a viscid oil. *Glycuronethiosemicarbazone*,



$$OH\cdot CH\left\langle\begin{matrix}CH(OH)\\ CO\text{——}O\end{matrix}\right\rangle CH\cdot CH(OH)\cdot CH{:}N\cdot NH\cdot CS\cdot NH_2,$$

crystallises from water in fascicular groups of needles melting at 223°, and is insoluble in the ordinary organic solvents. *Glycuronediphenylhydrazone*, $C_6H_8O_5{:}N_2Ph_2$, crystallises in needles melting at 150°. Glycuroneoxime is converted by acetic anhydride and sodium acetate into the tetraacetyl derivative of the seminitrile of *d*-saccharic acid, which has not, however, been obtained pure.

Glycuronic acid forms characteristic salts with many of the alkaloids. The *cinchonine* salt, $C_6H_{10}O_7,C_{19}H_{22}N_2O$, crystallises in characteristic white needles melting at 204°, and has $[\alpha]_D$ +138·6°. The *quinine* salt softens at 175°, melts at 180°, and has $[\alpha]_D$ −80·1°. The *brucine* salt crystallises in very slender needles melting at 200°, and the *strychnine* salt closely resembles it.

Glycurone can readily be separated from the sugars by means of its thiosemicarbazone, and glycuronic acid by the aid of the cinchonine salt, whilst the acid is best detected in presence of the sugars by means of the *p*-bromophenylhydrazine compound. A. H.

Acidimetry of Aldehydes and Ketones. By A. ASTRUC and H. MURCO (*Compt. rend.*, 1900, **131**, 943—945).—A number of aldehydes and ketones of simple and mixed function were examined as to their behaviour towards the indicators helianthin A, phenolphthalein, and Poirrier's-blue.

The simple aliphatic and aromatic aldehydes are neutral towards all three indicators. Glyoxal, the only simple dialdehyde examined, reacts with one equivalent of alkali, but the process is slow. Halogenated aldehydes, such as chloral hydrate, chloral alcoholate, and bromal, are neutralised by one equivalent of alkali. Hydroxybutyraldehyde and aldehydic sugars are neutral towards all three indicators, whereas salicylaldehyde, *p*-hydroxybenzaldehyde, methylprotocatechuic aldehyde (vanillin), and methylenoprotocatechuic aldehyde (piperonal) are neutral towards helianthin but monobasic towards phenolphthalein or Poirrier's-blue.

The simple aliphatic and aromatic ketones are without action on either of the three indicators. Acetylacetone is exactly monobasic towards Poirrier's-blue, but behaves less definitely with phenolphthalein. The exact titration of methylacetylacetone is impossible with either of these indicators. Acetonylacetone is neutral. Chloroacetone and bromoacetophenone are neutral towards helianthin and monobasic towards phenolphthalein or Poirrier's-blue. The ketonic sugars are neutral. Pyruvic and lævulic acids are exactly monobasic towards phenolphthalein or Poirrier's-blue, but with helianthin the neutral point is reached before one equivalent of alkali has been added.

N. L.

Search for other Sugars than Xylose and Dextrose in the Products of the Hydrolysis of Wood from the Trunks of Trees. By FRANCIS H. STORER (*Bull. Bussey Inst.*, 1900, **2**, 437—467).—The author has submitted samples of wood from the trunks of the sugar maple (*Acer saccharinum*) and birch (*Betula populifolia*), and from the root of the former tree to the action of hydrochloric and sulphuric acids under various conditions, and determined the cupric-reducing and rotatory powers of the solutions thus produced, in order to obtain, if possible, indications of the presence in wood of substances hitherto undetected. Cotton cloth was also subjected to the same treatment. The results of these experiments led to the following conclusions.

When strong sulphuric acid is allowed to act on cellulose, and the product boiled with dilute acid, the whole of the cellulose is not readily converted into dextrose, as has been frequently stated.

The compounds which carbohydrates form with sulphuric acid are very difficult to decompose by long continued boiling, and, as a general rule, a considerable part of the organic matter with which the strong acid at first united is not changed into dextrose when subsequently boiled with the dilute acid; some part of this undecomposed substance remains admixed with the dextrose syrup, and tends finally to contaminate the solid dextrose. If the calcium or barium salts of these compounds of carbohydrates with sulphuric acid are boiled for a long time, some quantity of the salts is liable to remain undecomposed and render the dextrose syrup impure; when such syrups are concentrated, crystals of two kinds are obtained, one of which consists entirely of inorganic matter. Béchamp (*Ann. chim. phys.*, 1831, [ii], **48**, 502) appears to have mistaken the latter substance for sugar, and it is probably due to the same cause that Berthelot (*Ann. chim. phys.*, 1859, [iii], **55**, 293) was led to state that the dextrose from wood differs from all other dextroses.

The quantity of dextrose which is usually said to be obtainable from a given weight of cellulose is largely in excess of that observed by the author; such statements, however, are generally based merely on the reducing power of the product of hydrolysis, whereas in the solutions obtained, substances other than dextrose are present which are capable of reducing considerable quantities of Fehling's solution.

The portion of the product of hydrolysis which is insoluble in alcohol is usually regarded as 'dextrin,' but its high reducing power suggests the presence of a sugar analogous to *iso*maltose. If, however, pure dextrose is treated with sulphuric acid under conditions similar to those observed in the hydrolysis of wood, a part of the residue obtained is insoluble in alcohol, and resembles the 'dextrin' from wood; it may be, therefore, that in each case some of the dextrose is converted by the alcohol into the insoluble dextrose anhydride.

The difficulties attending the study of the hydrolysis of cellulose are greatly increased by the reversion of dextrose to dextrin which may occur in the process.

E. G.

Formation of Amino-alcohols. By Louis Henry (*Ber.*, 1900, **33**, 3169—3171. Compare this vol., i, 16, and Strauss, *ibid.*, 17).—A number of amino-alcohols have been prepared by the reduction of the corresponding nitro-compounds with tin and hydrochloric acid, or from cyano-alcohols by reduction with sodium and alcohol. They are somewhat viscid liquids with a fishy odour, and dissolve in water, but, with the exception of methyl-α-aminoethylcarbinol, are insoluble in ether:

	Boiling point.	Sp. gr.
β-Aminoethyl alcohol, $OH\cdot CH_2\cdot CH_2\cdot NH_2$	171°	1·022 at 20°
γ-Aminopropyl alcohol, $OH\cdot[CH_2]_3\cdot NH_2$	187—188	1·020 at 12
δ-Aminobutyl alcohol, $OH\cdot[CH_2]_4\cdot NH_2$	206	0·967 at 12
β-Amino*iso*propyl alcohol, $OH\cdot CHMe\cdot CH_2\cdot NH_2$	160—161	0·973 at 18
Methyl-α-aminoethylcarbinol, $OH\cdot CHMe\cdot CHMe\cdot NH_2$	159—160	0·9423 at 18

When nitroacetone is kept for some time it turns brown, whereas nitroethyl alcohol remains colourless even when kept for some years.

J. J. S.

Hydrazides and Azoimides of Organic Acids. XVII. Synthesis of αγ-Diaminopropane and αζ-Diaminohexane from Glutaric and Suberic Acids respectively. By Theodor Curtius and Hans Clemm (*J. pr. Chem.*, 1900, [ii], **62**, 189—211).—*Glutaric dihydrazide*, $CH_2(CH_2\cdot CO\cdot NH\cdot NH_2)_2$, obtained by boiling hydrazine hydrate with ethyl glutarate, crystallises in silky leaflets which melt at 176°, reduces Fehling's solution, forms a colourless *hydrochloride*, and when shaken with benzaldehyde yields *dibenzylideneglutaric dihydrazide*, which crystallises from glacial acetic acid in small needles melting at 231—232°. *Glutaric diazoimide*, $CH_2(CH_2\cdot CO\cdot N_3)_2$, is obtained by adding a cold solution of sodium nitrite to a cooled solution of glutaric dihydrazide hydrochloride under ether; it is a clear, mobile, explosive oil with a suffocating odour, does not solidify at −15°, is decomposed by sodium hydroxide, yielding sodium azoimide; when treated with ethyl alcohol, it yields *diethyl trimethyleneurethane*, $CH_2(CH_2\cdot NH\cdot CO_2Et)_2$, which is a viscous oil boiling and decomposing at 290—300°, and solidifying to feathery crystals after standing in a freezing mixture for some time; when heated in a sealed tube at 100—110° for some hours, it yields trimethylenediamine hydrochloride. Glutaric diazoimide, when slightly warmed with water, explodes with the formation of small quantities of *trimethylenecarbamide* which melts at about 250°.

The corresponding suberic compounds were obtained by analogous methods. *Suberic dihydrazide*, $C_2H_4(CH_2\cdot CH_2\cdot CO\cdot NH\cdot NH_2)_2$, crystallises in large, colourless, lustrous leaflets which melt at 185—186°, and yields a *dibenzylidene* compound which crystallises in small, white needles and melts at 197°. *Suberic diazoimide* is obtained in compact crystals which melt at 25° and explode when heated further; when treated with alcoholic ammonia, it yields *suberamide*, which crystallises from alcohol and melts at 216°; when treated with aniline, it yields *hexamethylenedicarbanilide*, $C_6H_{12}(NH\cdot CO\cdot NHPh)_2$, which crystallises in long, thin, colourless prisms and melts at 220°; when treated with anhydrous alcohol, it yields *diethyl hexamethylenediurethane*,

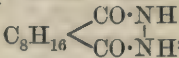
$$C_6H_{12}(NH\cdot CO_2Et)_2,$$

which crystallises in long, lustrous, colourless needles melting at 84°; with alcohol in the presence of water, it yields the *urethanecarbamide*, $CO(NH\cdot[CH_2]_6\cdot NH\cdot CO_2Et)_2$, which is a colourless, crystalline compound melting at 132°; when treated with water, it yields *hexamethylenecarbamide*, which crystallises in long, lustrous, colourless needles melting at 84°. *αζ-Diaminohexane dihydrochloride*, $C_6H_{12}(NH_2)_2,2HCl$, best prepared by the hydrolysis of diethyl hexamethyleneurethane with concentrated hydrochloric acid, crystallises in colourless needles, melts at 248°, and when treated with solid potash yields *αζ-diaminohexane* (hexamethylenediamine), which crystallises in silky, colourless leaflets, melts at 42°, boils at 100° under a pressure of 20 mm., is very hygroscopic, and absorbs carbon dioxide with the formation of a carbonate; it forms a *diacetyl* derivative which crystallises in small needles melting at 125—126°, a *dibenzoyl* derivative which crystallises in colourless plates melting at 157—158°, a *picrate*, $C_6H_{16}N_2,2C_6H_3O_7N_3$, which decomposes at about 200°, an *oxalate*, $C_6H_{16}N_2,2H_2C_2O_4,H_2O$, which melts and decomposes at 168°, a *platinichloride*, $C_6H_{16}N_2,H_2PtCl_6$, which decomposes between 222° and 224°, an *aurichloride* which crystallises in long, compact, lustrous yellow prisms, and a *mercurichloride*, $C_6H_{16}N_2,2HCl,4HgCl_2$, which crystallises in long leaflets and melts at 228—230°, all of which are analogous to the salts and derivatives of pentamethylenediamine; it dissolves uric acid, and has a very similar physiological action to piperazine and urotropine.

The melting points of the diamines, like those of the dibasic acids, of the normal hydrocarbons containing an even number of carbon atoms are higher than those containing an uneven number, whilst the boiling points increase regularly with number of carbon atoms.

R. H. P.

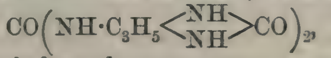
Hydrazides and Azoimides of Organic Acids. XVIII. Synthesis of αθ-Diaminooctane from the Azide of Sebacic Acid. By THEODOR CURTIUS and WILHELM STELLER (*J. pr. Chem.*, 1900, [ii], 62, 212—231).—*Sebacic dihydrazide*, $C_2H_4(\cdot[CH_2]\cdot_3CO\cdot NH\cdot NH_2)_2$, obtained by the action of hydrazine hydrate on diethyl sebacate, crystallises in lustrous, rhombic leaflets, melts at 184—185°, and when dry hydrogen chloride is passed into its anhydrous alcoholic solution, yields a *dihydrochloride* which forms rhombic crystals melting and decomposing about 250°; it condenses with benzaldehyde, forming *dibenzylidenesebacic dihydrazide*, which melts at 158—159°, forms a *tetrabenzoyl* derivative which melts at 250°, and when treated with an alcoholic solution of iodine (2 mols. iodine to 5 mols. dihydrazide) yields s-sec-*sebacic hydrazide*,



$C_8H_{16}<\begin{matrix}CO\cdot NH\\ | \\ CO\cdot NH\end{matrix}$,

which crystallises from alcohol and melts at 142°. *Sebacic diazoimide*, $C_8H_{16}(CO\cdot N_3)_2$, obtained by the action of nitrous acid on the dihydrazide, is a stable, colourless compound, which melts at 33—34°, and is not explosive. When treated with aniline, it yields *octomethylene dicarbamanilide*, $C_8H_{16}(NH\cdot CO\cdot NH\cdot Ph)_2$, which crystallises in flat, right-angled needles melting at 206—207°; when treated with water, *octomethylenecarbamide* is formed, which is an insoluble, bluish-white powder decomposing at 216°; when treated with moist ethyl alcohol, s-*dioctomethylenediethylurethanecarbamide*, $CO(NH\cdot[CH_2]_8\cdot NH\cdot CO_2Et)_2$, is obtained as an amorphous compound melting at 132—133°; when treated with absolute ethyl alcohol, *diethyloctomethylenediurethane*, $C_8H_{16}(NH\cdot CO_2Et)_2$, is formed, and crystallises in feathery aggregates melting at 78—80°; when treated with methyl alcohol, the corresponding *dimethylurethane* which melts at 114—115° is obtained.

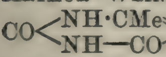
Octomethylenediamine dihydrochloride is best prepared by boiling either the diethyl- or dimethyl-urethane with concentrated hydrochloric acid for six hours. The derivatives and salts of octomethylenediamine are analogously constituted to those of hexamethylenediamine (see preceding abstract); the *dibenzoyl* derivative crystallises in silky prisms and melts at 140°, the *picrate* melts at 182—183°, the *oxalate* crystallises in lustrous, white laminæ and melts at 223°, the *mercurichloride* crystallises in pinkish aggregates and melts at 189—191°, the *aurichloride* forms microscopic crystals and melts at 188—189°; it also forms a characteristic *salt* with cadmium chloride, which crystallises in white aggregates from hydrochloric acid, and does not melt below 300°. When treated with nitrous acid, the diamine yields a greenish oil, which has the odour of octyl alcohol, and is probably *octomethyleneglycol*. R. H. P.

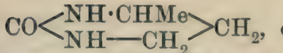
Hydrazides and Azoimides of Organic Acids. XIX. Synthesis of αβγ-Triaminopropane from Tricarballylic Acid. By THEODOR CURTIUS and AUGUST HESSE (*J. pr. Chem.*, 1900, [ii], 62, 232—246).—*Tricarballylic trihydrazide*, $C_3H_5(CO\cdot NH\cdot NH_2)_3$, obtained by the action of hydrazine hydrate on triethyl tricarballylate, is a crystalline substance melting at 195—196°, and forms a very soluble *trihydrochloride*, which melts and decomposes at 148°, a *tripicrate* which crystallises in small, yellow plates and melts at 173°, and condensation *products* with benzaldehyde and salicylaldehyde, which are white, microcrystalline substances melting at 218° and 205—206° respectively; when treated with nitrous acid, it yields *tricarballylic triazomide*, $C_3H_5(CO\cdot N_3)_3$, which is a clear, explosive oil; this, when treated with anhydrous ethyl alcohol, yields *triethyl glyceryltriurethane*, $C_3H_5(NH\cdot CO_2Et)_3$, which melts at 91—92°; when treated with water, *diglycerylcarbamide*,  $CO\left(NH\cdot C_3H_5<\begin{matrix}NH\\NH\end{matrix}>CO\right)_2$, which is a white, crystalline substance, is formed.

αβγ-Triaminopropane, $C_3H_5(NH_2)_3$ (compare Gabriel and Michels, Abstr., 1893, i, 31), is a colourless oil which boils at 92—93° under 9 mm. pressure, and forms a *trihydrochloride*, which is obtained by the hydrolysis of the urethane with hydrochloric acid, crystallises, with H_2O, in colourless, compact plates, and, when anhydrous, begins to sinter at 220°, and melts and decomposes about 250°; it forms an *aurichloride*, $C_3H_5(NH_2)_3,3HCl,AuCl_3$, which melts and decomposes at 210—212°, a *platinichloride*, $C_3H_5(NH_2)_3,3HCl,PtCl_4$, which crystallises in needles and decomposes at 220°, a *tripicrate*, which crystallises in long, yellow needles and does not melt below 270°, and a *tribenzoyl* derivative, which is a microcrystalline substance melting at 206—207°, and is particularly suited for the purification of the base, as when hydrolysed with strong hydrochloric acid it yields the hydrochloride in a pure state. R. H. P.

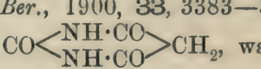
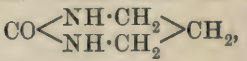
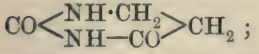
Formation of Canarin. By Bronislaw Pawlewski (*Ber.*, 1900, **33**, 3164).—Pure canarin is readily formed when ammonium persulphate is added gradually to a solution of ammonium thiocyanate contained in an open dish. When a woollen fabric is dipped in ammonium persulphate solution and then in ammonium thiocyanate and the operations repeated several times, the fabric becomes dyed intensely with canarin. J. J. S.

A Method of Preparing Hydantoin. By Carl D. Harries and Maurus Weiss (*Ber.*, 1900, **33**, 3418—3149).—The hydrochloride of the ethyl ester of glycine, when treated with potassium cyanate, is converted into *ethyl hydantoate*, which crystallises in compact needles, melts at 135°, and when treated with nitrous acid yields a *nitroso*-derivative melting at 66—67°; this ester, when heated at 135° for seven hours, or when warmed with 25 per cent. hydrochloric acid, is converted into hydantoin. The hydantoin formed by the latter method melts at 217—220° instead of at 215°. Quantitative yields are obtained in all the stages from glycine. R. H. P.

Electrolytic Reduction of Methyluracil. By Julius Tafel and Arthur Weinschenk (*Ber.*, 1900, **33**, 3378—3383).—Methyluracil,  $CO<\begin{matrix}NH\cdot CMe\\NH-CO\end{matrix}>CH$, was dissolved in 50 per cent. sulphuric acid and reduced electrolytically either at 15° or at 50°, between prepared lead electrodes (Abstr., 1900, ii, 588), with a current concentration of 120—150 amperes. The resulting liquid was freed from free sulphuric acid and evaporated under diminished pressure; the residue was extracted with boiling chloroform, in which *methyltrimethylene*-

carbamide,  $\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CHMe}\\ \mathrm{NH{-}{-}CH_2}\end{matrix}>\mathrm{CH_2}$, dissolved, whilst the sulphate of *αγ-diaminobutane,* $NH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot NH_2$, remained behind. Methyltrimethylenecarbamide melts at 200—202°, and is neutral in reaction; it forms a *picrate,* which was analysed; it is not easily hydrolysed, but when heated with concentrated hydrochloric acid at 200° (or less well with 30 per cent. sulphuric acid), it loses carbon dioxide and forms diaminobutane. αγ-Diaminobutane boils at 140·5—141·5° under 738 mm. pressure, and has a sp. gr. 0·86; its *hydrochloride,* which melts at 170—172°, and *picrate,* which is very insoluble and explodes when heated, were analysed.

These reactions afford a convenient means of preparing αγ-diaminobutane. Methyluracil is reduced electrolytically in the manner described; the resulting liquid is freed from so much sulphuric acid that three parts of the latter still remain for every 1 part of methyluracil, the liquid is concentrated until only 10 c.c. remain per 1 gram of uracil, and the residue is heated for 6 hours at 200°. C. F. B.

Electrolytic Reduction of Barbituric Acid. By JULIUS TAFEL and ARTHUR WEINSCHENK (*Ber.*, 1900, **33**, 3383—3387).—Barbituric acid, or malonylcarbamide,  $\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}>\mathrm{CH_2}$, was reduced electrolytically at 16—21°, and the product worked up as in the case of methyluracil (preceding abstract). The residue after the evaporation contained trimethylenecarbamide,  $\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CH_2}\\ \mathrm{NH\cdot CH_2}\end{matrix}>\mathrm{CH_2}$, and *hydrouracil,*  $\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CH_2}\\ \mathrm{NH{-}CO}\end{matrix}>\mathrm{CH_2}$; the latter remained behind when the residue was extracted with cold water, whilst the trimethylenecarbamide dissolved, and could be recovered from the solution by means of its *picrate,* which is almost insoluble in cold water. Hydrouracil melts at 274°, and in small quantities sublimes unchanged; it does not dissolve more readily in dilute hydrochloric acid than in water, but it does so in aqueous sodium or barium hydroxide; from these solutions, it is precipitated by carbon dioxide. C. F. B.

Nitration of the Disubstitution Derivatives of Benzene. By CHARLES CLOEZ (*Compt. rend.*, 1900, **131**, 899—901).—When a disubstitution derivative of benzene contains a basic group NH_2 or NR_2, and the second group is neutral (Me,Cl) feebly acid (OH) or acid (CO_2H), nitration takes place in the para- or ortho-position with respect to the amino-group. Nitration in the meta-position is obtained only in presence of a large excess of sulphuric acid.

When the benzene derivative contains an OH group with the groups Me, Cl, NO_2, or COH, nitration takes place in the ortho- and para-positions, but if the hydroxyl group is converted into an alkyloxy-group, nitration will take place also in the meta-position. With the derivatives $CO_2H : OH = 1 : 3$, three compounds are obtained with the NO_2 group in the position 2 or 4 or 5.

When the derivative contains a Me or Cl group with a NO_2, CO_2H, or COH group, nitration takes place in the ortho- or para-position with respect to the Cl or Me group.

With *o*-nitro- or *p*-nitro-benzoic acid, the second nitration takes place in the meta- or para-position with respect to the first nitro-groups.

C. H. B.

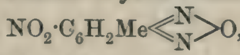
Nitro-derivatives of *o*-Dinitrosotoluene and *o*-Dinitrosoxylene. By THEODOR ZINCKE and P. DROST (*Annalen*, 1900, **313**, 299—316. Compare Abstr., 1899, i, 751).—*Nitro-*o*-dinitrosotoluene* [$Me : NO_2 : (NO)_2 = 1 : 2 : 3 : 4$ or $1 : 6 : 3 : 4$], prepared from 3 : 4-dinitrosotoluene and fuming nitric acid, crystallises in pale yellow needles which melt and decompose at 164°; it is also formed when the imide of *o*-nitro-*p*-toluidine is added to fuming nitric acid and the product heated in a brine bath. 2 : 6-*Dinitro*-3 : 4-*dinitrosotoluene*, obtained by the action of fuming nitric acid on a solution of the nitro-derivative in concentrated sulphuric acid, crystallises from concentrated nitric acid in silky yellow needles melting and decomposing at 133°.

*Nitro-*o*-dinitrosotoluene* [? $Me : (NO)_2 : NO_2 = 1 : 3 : 4 : 5$], produced when dinitro-*p*-diazotolueneimide is heated at 110°, crystallises from glacial acetic acid in lustrous, yellow leaflets melting at 145°; *dinitro-*p*-diazotolueneimide*, formed on dissolving nitrodiazotolueneimide in fuming nitric acid, crystallises from alcohol in colourless needles and melts at 97°.

5-*Nitro*-2 : 3-*dinitrosotoluene* crystallises from alcohol in yellow leaflets and melts at 70°. 5-*Nitro-*o*-diazotolueneimide* [5-*nitrotoluene*-2-*azoimide*], $NO_2\cdot C_6H_3Me\cdot N_3$, melts at 69°, and when treated with fuming nitric acid is converted into 3 : 5-*dinitrotoluene*-5-*azoimide*, which crystallises from alcohol in pale yellow needles, and melts at 61°; the latter substance yields 5-nitro-2 : 3-dinitrosotoluene when heated on the water-bath.

Nitrodinitrosotoluene [? $Me : (NO)_2 : NO_2 = 1 : 2 : 3 : 4$], obtained by dissolving 2 : 3-dinitrosotoluene in fuming nitric acid, forms pale yellow, feathery crystals and melts at 162°; a mixture of concentrated sulphuric and nitric acids converts it into *dinitrodinitrosotoluene* [? $Me : (NO)_2 : (NO_2)_2 = 1 : 2 : 3 : 4 : 6$], which melts and decomposes at 122—123°.

*Dinitro-*m*-xyleneazoimide* [$Me_2 : N_3 : (NO_2)_2 = 1 : 3 : 4 : 5 : 6$ or $1 : 3 : 4 : 2 : 5$], produced by the action of fuming nitric acid on 3 : 4 : 5-nitro-*m*-xyleneazoimide, crystallises from alcohol in white leaflets melting at 82°; when heated at 110°, it yields *nitrodinitroso-xylene*, which crystallises from alcohol in yellow needles, and melts at 116°.

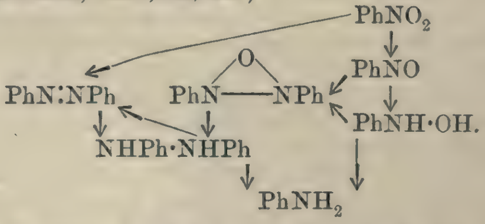


Nitrotolylenefurazan, $NO_2\cdot C_6H_2Me\left\langle\!\left\langle\begin{matrix}N\\N\end{matrix}\right\rangle\!\right\rangle O$, prepared from 1 : 3 : 4-tolylenefurazan and nitric acid, crystallises in long, yellowish needles, and melts at 83°.

Dinitroaminocresol [? $Me : OH : (NO_2)_2 : NH_2 = 1 : 2 : 3 : 5 : 4$], formed when dinitro-*p*-tolueneazoimide, is dissolved in concentrated sulphuric acid, crystallises from boiling water in small, red needles, and melts at 172°, when it decomposes; the *acetyl* derivative forms yellow crystals, and melts at 171°. *Dinitroaminocresol* [$Me : OH : (NO_2)_2 : NH_2 = 1 : 4 : 3 : 5 : 2$ or $1 : 6 : 3 : 5 : 2$], obtained from dinitro-*o*-tolueneazoimide, crystallises from boiling water in small, yellow needles.

The *compound* $C_7H_7O_5N_3$, a bye-product of the nitration of nitro-*p*-tolueneazoimide, separates from alcohol in lustrous crystals, and melts, decomposing, at 146°; the *acetyl* derivative melts and evolves gas at 142°. M. O. F.

Electro-chemical Reduction of Mononitro-compounds in slightly Alkaline Solutions. By KARL ELBS (*Zeit. Electrochem.*, 1900, 7, 133 and 144).—The author gives a *résumé* of the results obtained in the reduction of 56 mononitro-compounds by the method described by him (Abstr., 1899, i, 270). He shows that, in every case, these results are in harmony with the following representation of the electrolytic reduction of nitrobenzene, due to Haber and Schmidt (*Zeit. physikal. Chem.*, 1900, **32**, 271):



The vertical arrows indicate electrolytic reductions, the slanting ones indicate purely chemical reactions which take place between the different products. The nature and relative quantities of the final products will, of course, depend on the properties of the compound undergoing reduction. *p*-Nitroaniline, for example, yields *p*-phenylenediamine, owing to the fact that the nitroso-compound first formed changes very readily into quinoneimide oxime, which can only lead to the diamine; *m*-nitroaniline, on the other hand, yields *m*-diaminoazobenzene, owing to the fact that the meta-compounds have no tendency to form quinone derivatives. The nitroso- and hydroxylamine compounds formed by the direct reduction, therefore, react yielding the azoxy-compound which is further reduced.

The azo-compound is always formed by oxidation of the hydrazo-compound; in cases, therefore, where the latter is not readily formed the azo-compound is not produced.

The dinitro-compounds behave in an entirely different manner.

T. E.

Isolation of Sulphonic Acids by Vacuum Distillation. By FRIEDRICH KRAFFT and W. WILKE (*Ber.*, 1900, **33**, 3207—3209. Compare Krafft and Roos, Abstr., 1892, 1219.)—In addition to the sulphonic esters, a number of sulphonic acids can be purified by distillation, when the cathode-light vacuum is used (Abstr., 1896, ii, 464). The boiling points and melting points of the acids are as follows:

	M. p.	B. p. at 0 mm.	Height of vapour column.
Benzenesulphonic acid	66°	135°	90 mm.
Toluene-*p*-sulphonic acid	35	147	65 ,,
p-Xylenesulphonic acid............	48	149	55 ,,
p-Chlorobenzenesulphonic acid...	68	148	60 ,,
p-Bromobenzenesulphonic acid...	103	155	60 ,,

T. M. L.

αβ-Dichlorostyrenes and some Acetylenes. By FRANZ KUNCKELL and R. KORITZKY (*Ber.*, 1900, **33**, 3261—3264. Compare Abstr., 1900, i, 638).—*αβ-Dichloro*-p-*ethylstyrene*, $C_6H_4Et\cdot CCl\colon CHCl$, prepared by heating chloroacetyl-*p*-ethylbenzene with phosphorus pentachloride, is a colourless oil boiling at 265°; it has a sp. gr. 1·2565 at 17°. p-*Ethylphenylchloroacetylene*, $C_6H_4Et\cdot C⋮CCl$, obtained by boiling the preceding compound with alcoholic potassium hydroxide, is a yellow oil with an odour of oranges boiling at 160—170° under 35 mm. pressure; it has a sp. gr. 1·0871 at 17°. p-*Ethylphenylacetylene*, $C_6H_4Et\cdot C⋮CH$, readily produced by treating *αβ*-dichloro-*p*-ethylstyrene with sodium in ethereal solution, possesses an odour of anise, boils at 110° under 10 mm. pressure and has a sp. gr. 0·9086 at 18°.

p-*Cumyl chloromethyl ketone*, which crystallises from alcohol in needles and melts at 55—56°, yields *αβ-dichloro*-p-iso*propylstyrene*, a colourless oil boiling at 190—200° under 23 mm. pressure and having a sp. gr. 1·2736 at 17°.

p-iso*Propylphenylchloroacetylene*, $CHMe_2\cdot C_6H_4\cdot C⋮CCl$, a yellow oil boiling at 170—180° under 30 mm. pressure, has a sp. gr. 1·0852 at 17°. p-iso*Propylphenylacetylene*, a liquid having an ethereal odour, boils at 110—120° under 10 mm. pressure and has a sp. gr. 0·9124 at 17°. *αβ-Dichloro*-2 : 4 : 6-*trimethylstyrene*, $C_6H_2Me_3\cdot CCl\colon CHCl$, is a colourless oil boiling at 285—289° under atmospheric pressure; it has a sp. gr. 1·1998 at 17°.

2 : 4 : 6-*Trimethylphenylchloroacetylene*, $C_6H_2Me_3\cdot C⋮CCl$, a pale yellow oil boiling at 180—190° under 20 mm. pressure, has a sp. gr. 1·0349 at 18°. 2 : 4 : 6-*Trimethylphenylacetylene*, $C_6H_2Me_3\cdot C⋮CH$, has an ethereal odour and boils at 168—175° under 20 mm. pressure; it has a sp. gr. 0·8731 at 17°.

Cymyl chloromethyl ketone, $CHMe_2\cdot C_6H_3Me\cdot CO\cdot CH_2Cl$, crystallises from alcohol in needles and melts at 18—20°. *αβ-Dichloro*-2 (or 5)-*methyl*-5 (or 2)-iso*propylstyrene*, $CHMe_2\cdot C_6H_3Me\cdot CCl\colon CHCl$, obtained from the preceding ketone, is a colourless oil boiling at 268° under atmospheric pressure and having a sp. gr. 1·1296. 2 (or 5)-*Methyl*-5 (or 2)-iso*propylphenylchloroacetylene*, $CHMe_2\cdot C_6H_3Me\cdot C⋮CCl$, a yellow oil, boils at 215° under 40 mm. pressure and has a sp. gr. 1·0512 at 17°. 2 (or 5)-*Methyl*-5 (or 2)-iso*propylphenylacetylene*, $CHMe_2\cdot C_6H_3Me\cdot C⋮CH$, boils at 128—130° under 50 mm. pressure and has a sp. gr. 0·8882 at 17°.

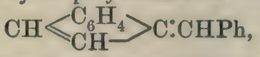
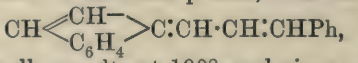
The sodium derivatives of the above unchlorinated acetylene, obtained in ethereal solution, are very unstable substances, being decomposed even by rubbing on a porous tile; water converts them into the corresponding acetylene and sodium hydroxide.

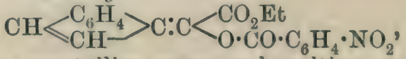
G. T. M.

Some Chloromethoxystyrenes. By FRANZ KUNCKELL and K. ERAS (*Ber.*, 1900, **33**, 3264—3265. Compare preceding abstract).—*αβ-Dichloro*-p-*methoxystyrene*, $OMe\cdot C_6H_4\cdot CCl\colon CHCl$, prepared from chloroacetylanisole and phosphorus pentachloride, is a colourless oil boiling at 155° under 12 mm. and at 268° under atmospheric pressure; it solidifies on cooling and has a sp. gr. 1·291 at 18°.

Bisdichloroethyleneanisole, $OMe\cdot C_6H_3(CCl\colon CHCl)_2$, obtained from di-chloroacetylanisole boils at 160—170° under 17 mm. pressure and has a sp. gr. 1·460 at 21°.

In the case of these methoxystyrenes, the removal of hydrogen chloride by alcoholic potash takes place only in sealed tubes; sodium fails to withdraw the halogen atoms even at the temperature of the water-bath. G. T. M.

Condensation Products of Indene. By JOHANNES THIELE (*Ber.*, 1900, **33**, 3395—3401).—The so-called condensation product obtained by Marckwald (Abstr., 1895, i, 535) from indene and benzaldehyde is shown to be the additive product hydroxybenzylbenzylideneindene, $C_{23}H_{18}O$, and Marckwald's acetate, produced by the action of acetyl chloride, is its chloro-derivative, $C_{23}H_{17}Cl$, which with moist silver oxide yields the hydroxy-compound, and when reduced with zinc dust and acetic acid yields a colourless, crystalline *compound*, $(C_{23}H_{18})_x$, which melts at 212—213°, and is probably a polymeride of benzylbenzylideneindene. *Benzylideneindene*,  $\mathrm{CH}<\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{CH}-\end{matrix}>\mathrm{C{:}CHPh}$, obtained in small quantities by the condensation of benzaldehyde and indene in the presence of alcoholic potash, crystallises in yellow leaflets, melts at 88°, and with concentrated sulphuric acid gives a yellowish-green coloration. Indene and cinnamaldehyde condense readily in the presence of alcoholic potash, with the formation of *cinnamylideneindene*,  $\mathrm{CH}<\begin{matrix}\mathrm{CH}-\\ \mathrm{C_6H_4}\end{matrix}>\mathrm{C{:}CH{\cdot}CH{:}CHPh}$, which crystallises in yellowish-red needles, melts at 190°, and gives a brown coloration with concentrated sulphuric acid, and an additive *compound*, $C_{27}H_{22}O$, which is analogous to hydroxybenzylbenzylideneindene, crystallises in slender, yellow needles, melts at 160—161°, and gives a green coloration with sulphuric acid. Ethyl indeneoxalate and *p*-nitrobenzoyl chloride condense in acetone solution in the presence of pyridine, forming *ethyl* p-*nitrobenzoylindeneoxalate*,



$$\mathrm{CH}<\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{CH}-\end{matrix}>\mathrm{C{:}C}<\begin{matrix}\mathrm{CO_2Et}\\ \mathrm{O{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2}\end{matrix},$$

which is a yellow, crystalline compound melting at 113—114°; the corresponding *benzoyl* compound is a red oil. *Indeneoxalic acid*, obtained by the careful hydrolysis of the condensation product of ethyl oxalate and indene, crystallises in small, lustrous, red prisms and melts and decomposes at 153—154°. R. H. P.

The Phenanthrene Series: Action of Nitrous Acid on Phenanthrene. By JULIUS SCHMIDT (*Ber.*, 1900, **33**, 3251—3260).—*Nitrodihydrophenanthrene oxide*, $O(C_{14}H_{10}{\cdot}NO_2)_2$, obtained in colourless, cubical crystals by saturating a benzene solution of phenanthrene with the fumes evolved from arsenious oxide and nitric acid, melts at 154—155°; it is extremely insoluble in the organic solvents, and, when recrystallised from benzene, separates in transparent prisms containing 1 mol. of benzene and melting at 134—135°. The substance gives the Liebermann reaction for nitroso-compounds, and on treatment with sodium methoxide yields a *nitrophenanthrene* melting at 116—117°, which is not identical with the mononitro-derivatives obtained by the direct nitration of the hydrocarbon.

Bismononitrodihydrophenanthrene, $NO_2\cdot C_{14}H_{10}\cdot C_{14}H_{10}\cdot NO_2$, which separates from the benzene mother liquor in the preceding experiment, consists of small needles melting at 199—200°, and crystallises from alcohol in pyramidal prisms; it also gives the Liebermann reaction, and develops a brownish-green coloration with cold concentrated sulphuric acid, which becomes deep green on warming, and changes to yellowish-brown on the addition of alkali.

Mononitrobisphenanthran (*mononitrobisdihydrophenanthrylene*),

$$C_{14}H_{10}\colon C_{14}H_9\cdot NO_2,$$

produced by heating the preceding compound for 10 minutes at 200—205°, crystallises from benzene in lustrous, yellow prisms and melts at 210—212°. The author proposes to employ the term "phenanthran" for the bivalent radicle, $C_{14}H_{10}$, derived from dihydrophenanthrene, and the preceding compound is named in accordance with this nomenclature.

Dinitrobisphenanthran, $NO_2\cdot C_{14}H_9\colon C_{14}H_9\cdot NO_2$, results from the action of sodium ethoxide on bismononitrodihydrophenanthrene; it slowly decomposes at 300° and has not been obtained crystalline owing to its insolubility in the ordinary solvents.
G. T. M.

Preparation of Triphenylchloromethane. By Moses Gomberg (*Ber.*, 1900, **33**, 3144—3149; *J. Amer. Chem. Soc.*, 1900, **22**, 752—757. Compare E. and O. Fischer, Abstr., 1879, 384).—The triphenylmethane obtained by so many authorities by the action of benzene on carbon tetrachloride in the presence of aluminium chloride is due to a secondary decomposition of the triphenylchloromethane, which is the first product formed. A 70—87 per cent. yield of the latter may be obtained by heating together carbon tetrachloride, benzene, and aluminium chloride, and at the end of the reaction running the well cooled mixture on to a large quantity of powdered ice contained in a vessel surrounded by a good freezing mixture.

For a good yield, it is essential that the original substances should be thoroughly dry, and that the product should never be left in contact with water for any length of time.
J. J. S.

Triphenylmethyl. An Instance of Tervalent Carbon. By Moses Gomberg (*Ber.*, 1900, **33**, 3150—3163; *J. Amer. Chem. Soc.*, 1900, **22**, 757—771).—Triphenyl-bromo- or -chloro-methane is not acted on by metallic sodium, but zinc, mercury, or "molecular" silver remove the bromine or chlorine and, in the absence of air the unsaturated hydrocarbon *triphenylmethyl*, CPh_3, is quantitatively formed, but when air is not completely excluded, a considerable amount of *triphenylmethyl peroxide*, $CPh_3\cdot O\cdot O\cdot CPh_3$, is produced.

The author recommends the action of pure powdered zinc on a benzene solution of the chloro-compound, the operation being conducted in an apparatus free from rubber or cork connections. When the benzene solution is concentrated at 30—35° in an atmosphere of dry carbon dioxide, a solid residue of the unsaturated hydrocarbon is left; it does not melt at 60°, dissolves readily in benzene or carbon disulphide, and when a solution is kept for several weeks large, transparent crystals are deposited ; it has not been found possible to obtain these in a pure form, as they rapidly absorb oxygen.

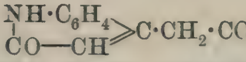
Triphenylmethyl peroxide is readily produced when the hydrocarbon is left exposed to the atmosphere, when air is aspirated through a benzene solution of the hydrocarbon, or when the benzene solution is treated with an aqueous solution of sodium peroxide. It is only sparingly soluble in the usual solvents, but may be crystallised from chloroform or carbon disulphide in the form of six-sided plates melting at 185—186° ; it is stable in the air but slowly decomposes when its solutions are boiled. When dissolved in cold concentrated sulphuric acid, it gives a yellow solution which quickly darkens, and on dilution triphenylcarbinol is precipitated. When nitrated, it yields *hexanitrotriphenylmethyl peroxide*, $O_2[C(C_6H_4{\cdot}NO_2)_3]_2$, melting at 210° and sparingly soluble in most solvents.

Triphenyliodomethane, CPh_3I, is readily obtained when a carbon disulphide solution of the unsaturated hydrocarbon is treated at 0° with a solution of iodine in the same solvent, and is best isolated in an atmosphere of dry carbon dioxide. It is unstable, readily darkens and loses iodine, melts at about 135°, and by water, especially in the presence of alkalis, is transformed into the carbinol ; boiling with alcohol converts it into triphenylmethane. The corresponding bromo- and chloro-compounds cannot be obtained by a similar process as bromine and chlorine form substitution as well as additive products.

J. J. S.

Action of Ethyl Acetonedicarboxylate on Aniline. By Emil Besthorn and E. Garben (*Ber.*, 1900, 33, 3439—3447).—*Ethyl-β-anilinoglutaconate*, $CO_2Et{\cdot}CH_2{\cdot}C(NHPh){:}CH{\cdot}CO_2Et$, prepared by the interaction of aniline and ethyl acetonedicarboxylate at the ordinary temperature, crystallises from methyl alcohol in transparent crystals melting at 87°, but melts at 97—98° when crystallised several times from dry ether ; the variation in melting point is explained by the supposition that two isomerides are produced ; the ester is insoluble in water but soluble in organic solvents, gives a yellowish-brown coloration with aqueous alcoholic ferric chloride, and is hydrolysed by cold dilute mineral acids.

Three products are formed when ethyl acetonedicarboxylate is heated with aniline in a sealed tube at 100°. *Acetonedicarboxydianilide*, $CO(CH_2{\cdot}CO{\cdot}NHPh)_2$, crystallises from absolute alcohol in small, colourless needles, melts, evolving gas, at 155°, gives a violet coloration with ferric chloride, and dissolves without decomposition in cold dilute sodium carbonate ; concentrated sulphuric acid gives sulphanilic acid, but the anilide condenses in presence of 80 per cent. acid on the water-bath to 2-quinolone-4-acetic acid. The *monoanilide* of *ethyl β-anilinoglutaconate*, $NHPh{\cdot}CO{\cdot}CH_2{\cdot}C(NHPh){:}CH{\cdot}CO_2Et$, separates from methyl alcohol in well-formed crystals, and when crystallised from dry ether melts at 129—130° ; with ferric chloride, it gives a yellowish colour, rapidly passing to violet as the compound is hydrolysed by the acid of the ferric chloride. The *monoanilide* of *ethyl acetonedicarboxylate*, $NHPh{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$, which is best prepared by the action of cold dilute hydrochloric acid on the preceding compound, crystallises from dry ether, melts at 75—76°, dissolves slightly in hot water and separates on cooling in minute felted needles; it dissolves unchanged in cold dilute sodium hydroxide, and can be reprecipitated at first by carbon dioxide, but hydrolysis of the ester gradually takes place; it is converted into 2-quinolone-4-acetic acid by warming with concentrated sulphuric acid during 2 hours on the water-bath.



2-*Quinolone-4-acetic acid*, $\left.\begin{array}{l}NH\cdot C_6H_4\\ \mid \\ CO\text{—}CH\end{array}\right>C\cdot CH_2\cdot CO_2H$, is only slightly soluble in water and organic solvents, crystallises from hot water in white, felted needles, melts, evolving gas, at 205—206°, and by further heating is converted completely into lepidone and carbon dioxide. The *ethyl* ester, $C_{13}H_{13}O_3N$, crystallises from benzene in colourless, flat needles, melts at 172—173°, and forms soluble crystalline salts with mineral acids. T. M. L.

Anilides of Alkylsulphonacetic Acids. By W. Grothe (*Arch. Pharm.*, 1900, **238**, 587—600).—Chloroacetyl derivatives of amines, $NHR\cdot CO\cdot CH_2Cl$, were prepared by mixing chloroacetic acid with the amine and cooling well, after which the product was mixed with excess of phosphoric oxide. In the case of methylaniline, chloroacetyl chloride was added to the well-cooled amine; indeed, this method is preferable in all cases for work on any but quite a small scale. There were prepared (the temperatures given are melting points): the *chloroacetyl* derivatives of aniline; *o*-and *p*-toluidine; 1:3:4-*xylidine*, 109°; 1:2:5-*xylidine*, 153°; p-*phenetidine*, 148°; *methylaniline*, 70°.

These chloroacetyl derivatives form sulphonacetyl compounds, $NHR\cdot CO\cdot CH_2\cdot SO_2\cdot R'$, when boiled with sodium benzene- or *p*-toluenesulphinate in alcoholic solution. When these compounds are boiled with 10 per cent. alcoholic potash, they are hydrolysed in all cases to the amine, NH_2R, carbon dioxide, and a sulphone, $CH_3\cdot SO_2\cdot R'$. Those prepared are: the *phenylsulphonacetyl* and p-*tolylsulphonacetyl* derivatives of *aniline*, 142° and 168° respectively; o-*toluidine*, 150° and 129°; p-*toluidine*, 153° and 157°; 1:3:4-*xylidine*, 141° and 153—154°; 1:2:5-*xylidine*, 143° and 160°; p-*phenetidine*, 151° and 156°; *methylaniline*, 125° and 112°. C. F. B.

Action of Potassium Hydrosulphide, Potassium Cyanide, and Potassium Thiocyanate on Chloroacetanilides. By W. Grothe (*Arch. Pharm.*, 1900, **238**, 600—614).—When potassium hydrosulphide is added gradually to a chloroacetanilide, $NHR\cdot CO\cdot CH_2Cl$, both in alcoholic solution, a dianilide of thiodiglycollic acid, $(NHR\cdot CO\cdot CH_2)_2S$, is obtained. In this way were prepared (the numbers given are melting points): *thiodiglycollyl* derivatives of aniline; o-*toluidine*, 190°; p-*toluidine*, 194°; 1:3:4-*xylidine*, 194°; 1:2:5-*xylidine*, 210°; p-*phenetidine*, 221°; *methylaniline*, 115°.

By oxidation with potassium permanganate in acetic acid solution, these derivatives can be converted into sulphones, $(NHR\cdot CO\cdot CH_2)_2SO_2$; the yield is not always good, however. There were prepared: *sulphonodiacetyl* derivatives of *aniline*, 220—225°; o-*toluidine*, 225—226°; p-*toluidine*, 221°; 1:2:5-*xylidine*, 237°; p-*phenetidine*, 239°; *methylaniline*, 152°; from 1:3:4-xylidine the corresponding derivative could not be obtained.

By mixing the chloroacetanilides with potassium cyanide in aqueous alcoholic solution, cyanoacetanilides, $NHR\cdot CO\cdot CH_2\cdot CN$, can be obtained in some cases. There were prepared: *cyanoacetyl* derivatives of aniline; p-*toluidine*, 180°; 1 : 2 : 5-*xylidine*, 167°; methylaniline; the corresponding derivatives of *o*-toluidine, 1 : 3 : 4-xylidine, and *p*-phenetidine could not be obtained. When these derivatives are heated with hydrochloric or sulphuric acid, they are hydrolysed to the amine, NH_2R, carbon dioxide, acetic acid, and ammonia.

When chloroacetanilides are heated with potassium thiocyanate in alcoholic solution, they form thiocyanoacetanilides, $NHR\cdot CO\cdot CH_2\cdot SCN$. There were prepared: *thiocyanoacetyl* derivatives of aniline, 86—87°; o-*toluidine*, 102—103°; p-*toluidine*, 125—126°; 1 : 3 : 4-*xylidine*, 102°; 1 : 2 : 5-*xylidine*, 133°; p-*phenetidine*, 164—165°; *methylaniline*, 69°. C. F. B.

Action of Potassium Thiocyanate on Chloroacetanilides. By Gustav Frerichs and Heinrich Beckurts (*Arch. Pharm.*, 1900, **238**, 615—616).—The thiocyanoacetyl compounds prepared by Grothe (preceding abstract) are derived from thiocyanoacetic acid, with the exception of the methylanilide, which is derived from thiocarbiminoacetic acid. The products obtained from other secondary amines, for instance ethylaniline, are also thiocarbimino-derivatives. Compounds of primary amines with thiocarbiminoacetic acid, on the other hand, are very unstable. In one case, that of *thiocarbiminoacetyl*-p-*toluidide*, the compound could be prepared by allowing potassium thiocyanate to act on chloroacetyl-*p*-toluidide in alcoholic solution for a very short time only; if the solution is heated, this compound is transformed into thiocyanoacetyl-*p*-toluidide, which finally can be converted into *p*-tolylthiohydantoin. C. F. B.

Some Reactions of Substituted Anilines. By William Oechsner de Coninck (*Compt. rend.*, 1900, **131**, 945—946).—In this paper, a minute description is given of the various colour changes and precipitates produced when solutions of methylaniline, dimethylaniline, ethylaniline, and diethylaniline in 97 per cent. alcohol are mixed with dilute or concentrated solutions of cupric chloride, sulphate, or acetate, and also, in the case of methylaniline, with solutions of cobalt or nickel chloride. N. L.

Trinitrothymol and its Derivatives. By Guido Maldotti (*Gazzetta*, 1900, **30**, ii, 365—370).—Trinitrothymol, prepared by Lallemand (*Ann. Chim. Phys.*, 1857, [iii], **49**, 150), has the normal molecular weight in freezing phenol. The following derivatives have been prepared. The *benzoyl* compound, $OBz\cdot C_6MePr(NO_2)_3$, separates from alcohol in silky, pale yellow needles melting at 140° and boiling and decomposing at 250°; it dissolves slightly in water or light petroleum, and is very soluble in benzene, in which its cryoscopic behaviour is normal. The *acetyl* derivative crystallises from benzene in pale yellow scales or plates melting at 135°; it dissolves slightly in ether, more readily in light petroleum, and gives the normal molecular weight in benzene. The *ethyl* derivative is deposited from alcohol in rhomboidal, nacreous scales or rectangular prisms which melt at 75°; it is soluble in benzene, to which it gives the normal depression of freezing point. The *phenylhydrazine* salt separates from alcohol in orange-yellow needles decomposing at 145°; it behaves normally in freezing phenol solution. T. H. P.

Action of Nitrous Acid on α- and β-Naphthols. By Julius Schmidt (*Ber.*, 1900, **33**, 3244—3246. Compare this vol., i, 89).—2 : 4-Dinitro-α-naphthol is produced when an ethereal solution of α-naphthol is saturated with the gas evolved from arsenious oxide and nitric acid; β-naphthol, when similarly treated, yields the dinitro-β-naphthol melting at 195°. G. T. M.

Addition of Aldehydoaminic Bases to Naphthols. By Mario Betti [with Cesare Speroni] (*Gazzetta*, 1900, **30**, ii, 301—309).—The naphthols resemble the enolic form of ethyl acetoacetate in containing the grouping $\cdot CH\vdots C(OH)\cdot$ in their molecules; and further, they give, with aldehydoaminic bases, additive compounds similar to those obtained with ethyl acetoacetate.

Benzylideneanil-β-naphthol, $NHPh\cdot CHPh\cdot C_{10}H_6\cdot OH$, prepared from benzylideneaniline and β-naphthol, crystallises from alcohol in aggregates of lustrous, white needles which melt at 170° and are soluble in benzene; it is readily decomposed by cold dilute acid but is stable towards alkali hydroxides. The presence of a drop of piperidine seems to greatly accelerate its formation.

m-*Nitrobenzylideneanil-β-naphthol*, $NO_2\cdot C_6H_4\cdot CH(NHPh)\cdot C_{10}H_6\cdot OH$, separates from a mixture of benzene and light petroleum as a yellowish-white, crystalline powder melting at 152°.

Benzylidene-β-naphthylamine-β-naphthol, $C_{10}H_7\cdot NH\cdot CHPh\cdot C_{10}H_6\cdot OH$, separates from alcohol as a white, crystalline powder which melts at 175° and is slightly reddened by the action of light.

Benzylideneanil-α-naphthol, $C_{23}H_{19}ON$, is deposited by the addition of light petroleum to its benzene solution in white crystals melting at 142° to an orange-yellow liquid.

These compounds are insoluble in water and their alcoholic solutions give no coloration with aqueous ferric chloride, but in benzene solution they give a reddish-violet colour with absolute ethereal ferric chloride solution.

On mixing benzene solutions of benzylideneaniline and picric acid, yellow needles of *benzylideneaniline picrate*, $C_{19}H_{14}O_7N_4$, melting at 173° are obtained. T. H. P.

Condensation between β-Naphthol, Aldehydes, and Amines. By Mario Betti (*Gazzetta*, 1900, **30**, ii, 310—316).—Under suitable conditions, β-naphthol condenses with an aldehyde (2 mols.) and a primary amine (1 mol.) with elimination of $2H_2O$. The substances obtained in this way crystallise well, have a high melting point, can be boiled with 25 per cent. potassium hydroxide solution without undergoing change, whilst prolonged boiling with hydrochloric acid yields the aldehyde employed; they are probably oxyazine derivatives. No condensation occurs if the β-naphthol is replaced by phenol or by diethyl malonate; secondary amines cannot replace the primary nor can acetone be used instead of an aldehyde.

β-Naphthol, benzaldehyde, and ammonia yield in almost theoretical quantity a *compound*, $C_{24}H_{19}ON$, crystallising from alcohol in white needles which melt at 150° and are soluble in benzene; ethereal ferric chloride gives an intense reddish-violet coloration with the benzene solution. Fusion with potassium hydroxide yields ammonia, whilst long boiling with hydrochloric acid gives benzaldehyde and a *substance* separating in white needles. The *acetyl* derivative of the condensation product is deposited from alcohol in lustrous, white crystals melting at 188—189°, and in benzene solution gives no coloration with ferric chloride.

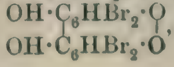
β-Naphthol, benzaldehyde, and aniline yield a *compound*, $C_{30}H_{23}ON$, which is readily soluble in benzene or chloroform, and separates from amyl alcohol in rosettes of small, white needles which begin to turn yellow at 160°, become orange-coloured at 185° and melt at 200°.

From β-naphthol, furfuraldehyde, and ammonia, a *compound*, $C_{20}H_{15}O_3N$, is obtained, which separates from alcohol in mammillary tufts of long, white needles melting at 115°; in benzene solution, it gives an intense violet coloration with ethereal ferric chloride.

β-Naphthol, valeraldehyde, and ammonia yield a *compound*, $C_{20}H_{27}ON$, crystallising from alcohol in tufts of long, lustrous white needles melting at 92°; its benzene solution gives an intense violet coloration with ethereal ferric chloride. T. H. P.

Etherification of Triphenylcarbinols by Alcohols. By Otto Fischer (*Ber.*, 1900, **33**, 3356—3357).—On dissolving the malachite-green base in boiling methyl alcohol, the *methyl ether*, $C_{24}H_{28}ON_2$, separates in white leaflets which rapidly become green, and melt at 150—151°; if the ether is dried rapidly over alkali, it does not subsequently become coloured. Acids, even acetic acid, remove the methoxyl group and yield salts of malachite-green. The corresponding *ethyl ether*, obtained at a temperature of 80—170°, forms concentrically grouped, colourless leaflets and melts at 162°; the *benzyl ether* is obtained only at temperatures above 140—150°, and forms white, silky needles, which when dried over alkali, retain their colour. It softens at 195°, melts at 198°, is coloured green by acids, and is decomposed by dilute sulphuric acid at 100° into benzyl alcohol and the sulphate of the malachite-green base. W. A. D.

Action of Nitric Acid on Tribromoguaiacol. By H. Cousin (*Compt. rend.*, 1900, **131**, 901—903).—When tribromoguaiacol, $OH\cdot C_6HBr_3\cdot OMe$, is oxidised with nitric acid in presence of acetic acid and some alcohol, it yields a compound, $C_{12}H_4O_4Br_4$, which forms orange-red, flattened needles, melts at 186—188°, and is insoluble in water, but dissolves readily in organic solvents. When treated with reducing agents, it yields a colourless compound, $C_{12}H_6O_4Br_4$, which forms prismatic crystals melting at 170—172°. With ferric chloride, its alcoholic solution gives a green coloration which changes to violet on addition of a trace of sodium carbonate. Both compounds yield diphenyl when treated with zinc dust. The red compound is a quinone which probably has the constitution



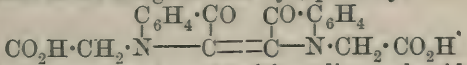
$$\begin{array}{l} OH\cdot C_6HBr_2\cdot O \\ \qquad\ \ | \qquad\qquad\ | \\ OH\cdot C_6HBr_2\cdot O \end{array}$$

, whilst

the colourless compound is the corresponding quinol. The action of nitric acid on tribromoguaiacol is similar to, but not identical with, its action on trichloroguaiacol (Abstr., 1900, i, 487). C. H. B.

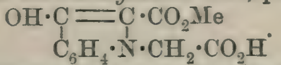
Anildiacetic-*o*-carboxylic Acid. By DANIEL VORLÄNDER and E. MUMME (*Ber.*, 1900, **33**, 3182—3183).—*Anildiacetic-o-carboxylic acid* (*diaceticanthranilic acid*), $CO_2H\cdot C_6H_4\cdot N(CH_2\cdot CO_2H)_2$, is obtained when anthranilic acid and excess of chloroacetic acid interact in neutral or alkaline solution. It crystallises from hot water in colourless tablets or leaflets and melts and decomposes at 212°. Its conductivity shows it to be powerfully acidic, but it cannot be titrated as a tribasic acid. It is not acted on by nitrous acid and its alcoholic solution is not coloured by ferric chloride. Unlike phenylglycinecarboxylic acid, it is readily esterified and with alcohol and sulphuric acid is converted into its *trimethyl ester*, $C_{11}H_3O_6NMe_3$, melting at 62°.

When the acid is heated with alkali hydroxides, it condenses to an indoxyl derivative which is oxidised by ferric chloride and strong hydrochloric acid to an indigotin-like dye, possibly



$$\begin{array}{l}\qquad\qquad\qquad\; C_6H_4\cdot CO \quad\; CO\cdot C_6H_4\\ CO_2H\cdot CH_2\cdot N{-\!\!-\!\!-}C{=\!\!=\!\!=}C{-\!\!-}N\cdot CH_2\cdot CO_2H\end{array}.$$

The trimethyl ester, on treatment with sodium ethoxide, is converted into the *methyl ester* of an *indoxylacetic acid*, possibly



$$\begin{array}{l} OH\cdot C{=\!\!=\!\!=}C\cdot CO_2Me \\ \qquad\; C_6H_4\cdot N\cdot CH_2\cdot CO_2H \end{array}.$$

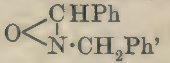
This is a well-crystallised substance and melts at 163°. A. L.

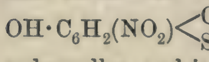
Esters of Acylphenylglycine-*o*-carboxylic Acids. By DANIEL VORLÄNDER and W. MEUSEL (*Ber.*, 1900, **33**, 3183—3185).—It has been shown by Vorländer and Weissbrenner (Abstr., 1900, i, 295) that the acetyl derivatives of phenylglycinecarboxylic acid are readily converted by acids or alkalis into indigotin. It was presumed that these esters might be derivatives of the type $C_6H_4{<}\begin{array}{c}C(OH)(OR)\\N(CO\cdot R)\end{array}{>}CH\cdot CO_2R$, the conversion of which into indigotin derivatives would be readily understood. Diethyl acetylphenylglycinecarboxylate may be prepared by the following different processes: 1, esterification of acetylphenylglycinecarboxylic acid; 2, acetylation of the esters of phenylglycinecarboxylic acid; and 3, action of ethyl iodide on silver acetylphenylglycinecarboxylate. Moreover, the isomeric monoethyl esters, $C_{13}H_{15}O_5N$, of acetylphenylglycinecarboxylic acid have been prepared; that obtained by partial hydrolysis of the diethyl ester melts at 130—132°, and that by partial esterification of the acid at 86—87°. These are not converted into indigo by dilute alkali and possess the normal constitutions,

$CO_2Et\cdot C_6H_4\cdot NAc\cdot CH_2\cdot CO_2H$ and $CO_2H\cdot C_6H_4\cdot NAc\cdot CH_2\cdot CO_2Et$.

The authors have finally proved that it is possible to detect indoxyl derivatives by means of warm 60 per cent. sulphuric acid, which converts them into indigotinsulphonic acids.

The authors draw the conclusion that the diethyl esters referred to are true derivatives of acetylphenylglycinecarboxylic acid and that their conversion into indigotin is preceded by intramolecular change into indoxyl derivatives. A. L.

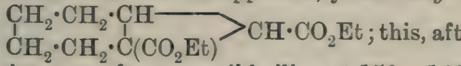
Action of Air and Water on β-Benzylhydroxylamine. By Eugen Bamberger and Bogdan Szolayski (*Ber.*, 1900, 33, 3193—3201. Compare Abstr., 1900, i, 531).—When pure air is passed through β-benzylhydroxylamine suspended in water for several months, it is converted into a dense, viscid oil, which finally becomes semisolid. The product contains benzaldoxime, benzaldehyde, and benzoic acid, benzyl*iso*benzaldioxime,  $O<\begin{matrix}CHPh\\ | \\ N\cdot CH_2Ph\end{matrix}$, benzaldoxime anhydride, $C_{14}H_{12}ON_2$, a neutral *substance* melting at 212—213°, benzylidenebenzhydrazide, $CHPh{:}N\cdot NH\cdot COPh$, dibenzoylhydrazine, $C_{14}H_{12}O_2N_2$. Bisnitrosobenzyl and azoxybenzyl could not be detected. As in the case of the oxidation of arylhydroxylamines, hydrogen peroxide is produced in considerable quantities. The neutral substance above mentioned crystallises in white, silky, felted needles, is very sparingly soluble in alcohol, and is indifferent towards bases and acids; its nature has not yet been ascertained. A. L.

Nitrosulphosalicylic Acids. By Robert Hirsch (*Ber.*, 1900, 33, 3238—3241).—Sulphosalicylic acid (Mendius, *Annalen*, 1857, 103, 45), prepared by the action of sulphuric acid on salicylic acid at 100°, can be salted out from its solution, and can be crystallised from a concentrated salt solution or from a little hot water. Contrary to Remsen's statement (Abstr., 1874, 1167; 1876, i, 594), the acid appears to be homogeneous, and only one potassium salt could be isolated. The nitration of salicylic acid (Hübner, Abstr., 1876, i, 593; 1879, 380) can be carried out smoothly by dissolving in sulphuric acid and adding a mixture of nitric and sulphuric acids until no marked rise of temperature occurs on mixing, the temperature being kept below 10°. A *nitrosulphosalicylic acid* can be prepared by nitrating sulphosalicylic acid at 30—40° by the method just described. The *barium* salt,  $OH\cdot C_6H_2(NO_2)<\begin{matrix}CO_2\\SO_3\end{matrix}>Ba$, crystallises from hot water in yellowish-red needles, and is almost insoluble in cold water. T. M. L.

Hydroxyphenylcinnamic Acid. By Marussia Bakunin (*Gazzetta*, 1900, 30, ii, 370—377).—The hydroxyphenylcinnamic acid melting at 120° prepared by Vandevelde (Abstr., 1898, i, 670) by the interaction of sodium hydroxyphenylacetate, benzaldehyde, and acetic anhydride is a mixture of cinnamic acid and the hydroxyphenylcinnamic acid melting at 181° obtained by Oglialoro (Abstr., 1881, 276). The *phenyl* ester melts at 107°, and not, as stated by Vandevelde, at 74°, which is the melting point of phenyl cinnamate. T. H. P.

Addition of Ketomethane Derivatives to Unsaturated Compounds. By Daniel Vorländer (*Ber.*, 1900, 33, 3185—3187).—It is often observed that ethyl sodiomalonate will unite with αβ-unsaturated ketones when benzene or ether is used as the diluent, but not if alcohol is used. The explanation of this appears to be that the reaction is a reversible one, and that the reverse change is slower in the non-hydroxylic solvents.

Thus, whilst ethyl pulegonemalonate may be prepared by heating pulegone with ethyl sodiomalonate dissolved in benzene or ether, it is broken up into these constituents when heated with an alcoholic solution of sodium ethoxide. In a similar manner, ethyl benzylidenebisbenzoylacetate is converted by alcoholic sodium ethoxide into ethyl benzoylacetate and ethyl benzylidenebenzoylacetate (compare also Dieckmann, Abstr., 1900, i, 623). A. L.

A Saturated Dicyclic Dicarboxylic Acid. By Wilhelm Braren and Eduard Buchner (*Ber.*, 1900, 33, 3453—3456).—*Ethyl* Δ′-*tetrahydrobenzoate* prepared from the corresponding acid (Aschan Abstr., 1891, 1481; 1893, i, 33) is an oil boiling at 206—208°, which, when heated with ethyl diazoacetate at 110—120° for 16—24 hours or until all the diazoacetate has disappeared, yields *ethyl* 1 : 2-*norcarandicarboxylate*,  $\begin{array}{l}CH_2\cdot CH_2\cdot CH\\ CH_2\cdot CH_2\cdot C(CO_2Et)\end{array}\!\!>CH\cdot CO_2Et$; this, after purification by distillation in steam, forms an oil boiling at 159—160° under 18 mm pressure; on hydrolysis with alcoholic potash, it yields cis-1 : 2-*norcarandicarboxylic acid*, $C_7H_{10}(CO_2H)_2$, together with an oily mass; the *cis*-acid melts at 152—153°, is readily soluble in water, alcohol or ether, and is not acted on by cold permanganate in alkaline solution. When boiled for 1½ hours with acetyl chloride, it yields the *anhydride*, $C_7H_{10}{:}C_2O_3$, which crystallises from carbon disulphide in colourless plates melting at 86—87°; when this is dissolved in sodium hydroxide solution and then acidified, it yields the original acid, and hence follows the *cis*-configuration of the latter. J. J. S.

Euxanthic Acid. By Carl Graebe (*Ber.*, 1900, 33, 3360—3362).—Although the potassium and sodium salts of euxanthic acid are of the type $C_{19}H_{17}O_{11}M$, the *silver* salt, precipitated from the potassium salt by silver nitrate, has the composition $C_{19}H_{15}O_{10}Ag$, derived from an anhydride of the acid; the *methyl* ester melting at 212°, and the *ethyl* ester, melting at 198°, prepared from the silver salt are of a similar type, $C_{19}H_{15}O_{10}\cdot R$. These esters, but not the free acid, combine directly with iodine (apparently 2 atoms at most) to form gelatinous, insoluble blue substances. With acetic anhydride, the esters yield colourless *acetyl* derivatives, derived not from the esters themselves, but from the anhydride, $C_{19}H_{16}O_{10}$; their composition remains to be determined. With benzoyl chloride, analogous substances are formed, the ultimate product being the *compound* $C_{19}H_{11}O_{10}Bz_5$.

W. A. D.

Lichens and their Characteristic Constituents. By Oswald Hesse (*J. pr. Chem.*, 1900, [ii], 62, 321—363. Compare Abstr., 1898, i, 531, 679; 1899, i, 381).—Specimens of usnic acid obtained from *Usnea ceratina*, *Cladonia rangifera* var. *silvatica*, *Parmelia caperata* and *Placodium saxicolum* var. *vulgare* gave $[\alpha]_D$ +494·1°, +494·6°, +492·2°, and +492·7° respectively, whilst that from *Cetraria pinastri* gave $[\alpha]_D$ −494·1°. When either *d*- or *l*-usnic acid is melted, it is instantly converted into the inactive modification. The *d*-acid melts at 195—197°, the *l*-acid at 197°, and the inactive form at 192—193°. The *potassium* salts of the *d*- and *l*-acids crystallise from water with $3H_2O$, and from alcohol with $1H_2O$. The inactive modifications obtained by fusion of the *d*- and *l*-acid respectively and that crystallised from a mixture of the two active forms are not absolutely identical, since the potassium salt crystallises in a different form in each case; the sodium salt, however, crystallises only in one form (compare Widman, Abstr., 1900, i, 235).

Ebullioscopic determination of the molecular weight of the substance obtained by the action of acetic anhydride on *d*-usnic acid (Hesse, Abstr., 1895, i, 298) gave 338—339, whilst a substance of the formula $(C_{18}H_{15}O_6)_2O$ requires 670; the author concludes that the supposed anhydride is a mixture of the lactone, $C_{18}H_{14}O_6$, and the *d*-acid.

A further examination of *Candelaria concolor* has shown that the 'dipulvic acid' previously described consists of pulvic anhydride together with a smaller quantity of calycin (compare Zopf, Abstr., 1899, i, 716). *Candelaria vitellina* obtained from four different sources furnished a substance composed of calycin and pulvic anhydride in varying proportions. *Sticta aurata* yields 'stictaurin,' $C_{18}H_{12}O_5$, which has the properties attributed to it by Zopf (*loc. cit.*). *Sticta Desfontainii a-munda* contains a substance melting at 232° which, when boiled with alcohol, furnishes calycin and ethylpulvic acid. If calycin (1 mol.) and pulvic anhydride (2 mols.) are dissolved in hot glacial acetic acid, a substance, $C_{18}H_{12}O_5,(C_{18}H_{10}O_4)_2$, separates which corresponds in every way with that obtained from *Sticta aurata* and crystallised from the same solvent; in one case, a substance, $C_{18}H_{12}O_5$, was produced resembling that obtained directly from *Sticta aurata* by extraction with ether. From a solution of calycin and pulvic anhydride in molecular proportion, a substance is obtained in brick-red needles which melts at 216—217°, and agrees in its characters with that yielded by *Candelaria vitellina.* If, however, more than 1 mol. of calycin is mixed with 1 mol. of pulvic anhydride, the excess of the former crystallises independently. The author concludes that the colouring matter of these lichens is not a definite single substance, but a mixture of calycin and pulvic anhydride in varying proportions, and that the calycin protects the anhydride from alteration.

Calycium chlorellum (*C. chlorinum*), yields vulpic acid and traces of leprarin.

Calycium flavum contains chrysocetraric acid and calycin.

When *Acolium tigillare* is extracted with ether, and the ethereal solution shaken with aqueous potassium hydrogen carbonate, the potassium salt of acolic acid separates, whilst rhizocarpic acid remains in solution. *Acolic acid* crystallises in small, white needles, melts and evolves gas at 176°, and is fairly soluble in alcohol, benzene, or chloroform when hot, but only sparingly at the ordinary temperature. The *ammonium*, *potassium*, and *barium* salts are described.

The investigation of the constituents of *Cetraria islandica* has been continued; the sample examined consisted chiefly of var. *vulgaris* and *platyna.* Lichenostearic acid is found to be a mixture of three acids, which the author terms α-, β-, and γ-lichenostearic acid.

α-Lichenostearic acid, $C_{18}H_{30}O_5$, is a monobasic acid which crystallises in prisms or plates, melts at 122—123°, gives $[\alpha]_D$ $+27{\cdot}9°$, and is soluble in benzene, chloroform, or hot glacial acetic acid; its *potassium, sodium, ammonium, barium,* and *silver* salts are described. The *methyl* ester, obtained by the action of methyl iodide on the potassium salt, crystallises in colourless needles, melts at 50·5°, and dissolves readily in alcohol or ether. The *ethyl* ester forms long, radiating crystals, melts at 29—30°, and is easily soluble in ether or alcohol. When α-lichenostearic acid is heated with aqueous barium hydroxide, it loses carbon dioxide and is converted into *lichestrone*, $C_{17}H_{30}O_3$, the lactone of lichestronic acid; lichestrone crystallises in white, lustrous plates, melts at 83—84°, is optically inactive, and dissolves readily in alcohol, ether, acetone, chloroform, benzene, or glacial acetic acid. It dissolves slowly in solution of potassium hydrogen carbonate, with formation of lichestronic acid; this change takes place more rapidly if potassium carbonate or hydroxide is employed.

Lichestronic acid, $C_{17}H_{32}O_4$, is monobasic; it crystallises from dilute acetic acid in prisms or plates, melts at 80°, is optically inactive, and dissolves very easily in alcohol, ether, benzene, or chloroform; its *barium* salt was prepared and analysed.

β-Lichenostearic acid, $C_{18}H_{30}O_5$, crystallises from acetic acid in leaflets, melts at 121°, gives $[\alpha]_D$ $+27·9°$, and by the action of baryta is converted into lichestrone; its *sodium*, *ammonium*, and *barium* salts are described. α- and β-Lichenostearic acids are readily distinguished by means of their ammonium salts; the ammonium salt of the former acid is sparingly soluble in cold water, whilst that of the latter acid is very easily soluble, and is precipitated in a gelatinous form on addition of excess of ammonium chloride.

γ-Lichenostearic acid, $C_{18}H_{30}O_5$, or $C_{19}H_{32}O_5$, melts at 121—122°, and gives $[\alpha]_D$ $+16·0°$; when its solution in benzene is heated, it is to a great extent polymerised. The *ammonium* salt is readily soluble in water; the *barium* salt is insoluble in water, whilst that of the β-acid is very easily soluble.

Paralichenostearic acid, $C_{20}H_{34}O_5$ (Abstr., 1899, i, 386), melts at 182°.

The foregoing acids are accompanied by smaller quantities of two other acids. The first of these has the composition $C_{18}H_{30}O_5$; when crystallised from alcohol, it melts at 140°, but if crystallised from glacial acetic acid, melts at 152°; its *barium* salt was prepared and analysed. The second acid is *dilichenostearic acid*, $C_{36}H_{60}O_{10}$, which melts at 272°, gives $[\alpha]_D$ $+15·2°$, and is easily soluble in ether, amyl alcohol, or hot chloroform, and sparingly in benzene, light petroleum, or hot alcohol; determination of the molecular weight by the boiling point method gave 659 ($C_{36}H_{60}O_{11}$ requires 652); its *sodium*, *ammonium*, and *barium* salts are described.

The author was unable to detect any phytosterol, or similar substance, among the constituents of *Cetraria islandica*. The lichenostearic acid described by Sinnhold (Abstr., 1899, i, 13), is probably the α-acid, whilst his lichenosterylic acid appears to be lichestrone.

E. G.

Compounds from Lichens. VII. By Wilhelm Zopf (*Annalen*, 1900, **313**, 317—344. Compare Abstr., 1899, i, 716).—*Lepraria latebrarum* (Ach.) yields roccellic acid, atranoric acid, and leprarin, which melts at 155°; methyl, ethyl, and propyl alcohols, under the influence of hydrochloric acid, convert leprarin into *leprarinin*, melting at 135°, *lepraridin*, melting at 120—121°, and *lepralin*, melting at 100°, respectively. *Gyrophora vellea* and *G. spodochroa* (Ehrh.) var. *depressa* contain gyrophoric acid, which in the former lichen is associated with *gyrophorin*; this crystallises from alcohol in minute, rhombic plates, and melts, evolving gas, at 189°. Usnic acid has been identified in *Ramalina thrausta* (Ach.), *Alectoria sarmentosa* (Ach.), *Cladonia deformis* (L.), *C. cyanipes* (Sommerfelt), and *Parmelia incurva* (Pers.). *Lecanora epanora* (Ach.) contains zeorin and *epanorin*, which crystallises from warm ether in lemon-yellow needles, and melts at 131—132°. *Parmelia Borreri* (Turn.) yields lecanoric acid, and *P. sorediata* (Ach.) contains diffusin; the greenish-yellow colour of *Rhizocarpon viridiatrum* (Flörke) is due to rhizocarpic acid.

The author has isolated salazinic acid and picrolichenin from *Pertusaria amara* (compare Hesse, Abstr., 1899, i, 383), and corrects his former statement to the effect that *Physcia caesia* (Hoffm.) contains hæmatomic acid. The compound in *Evernia furfuracea* (L.), at first thought to be erythrin, is now recognised as a new substance, *olivetoric acid*, $C_{27}H_{36}O_8$, which crystallises from 55 per cent. alcohol in long, silky needles, and melts at 141—142°; when heated with methyl alcohol in sealed tubes at 150°, it yields *olivetorinic acid*, which sinters at 65°, and melts at 88°. M. O. F.

Disulphones. V. Acetophenone and Benzophenone Disulphones. By Theodor Posner (*Ber.*, 1900, **33**, 3165—3168. Compare this vol., i, 14).—According to Baumann (*Ber.*, 1886, **19**, 2803) aromatic and aromatic-aliphatic ketones do not yield disulphones by conversion into mercaptoles and oxidation; the author has, however, succeeded in obtaining disulphones from acetophenone and benzophenone. *αα-Diethylthiol-α-phenylethane* (*acetophenonemercaptole*), $CMePh(SEt)_2$, is readily formed when hydrogen chloride is passed into an acetic acid solution of acetophenone and ethyl mercaptan. It is an oily compound, and on oxidation yields αα-diethylsulphone-α-phenylethane (acetophenonedisulphone) melting at 119—120° (corr.); this compound is identical with that described by Fromm (*Annalen*, 1889, **253**, 135) as melting at 100—101°.

Diethylsulphonediphenylmethane (*benzophenonedisulphone*),

$$CPh_2(SO_2Et)_2,$$

forms small, nodular crystals melting at 136—137° (corr.). J. J. S.

Action of Nitrous Acid on Benzoquinone. By Julius Schmidt (*Ber.*, 1900, **33**, 3246—3250).—*Nitroanilic acid benzoquinone*, $OH{\cdot}C_6(NO_2)_2{:}O_2{:}O_2{:}C_6H_4$, obtained by saturating a cooled ethereal solution of benzoquinone with the fumes evolved from nitric acid and arsenious oxide, crystallises in lustrous yellow prisms, and decomposes at 160°; it is readily soluble in acetone, ethyl acetate, or the alcohols, and dissolves only sparingly in chloroform, benzene, or toluene. An intense bluish-red coloration is developed on treating its alcoholic solution with ferric chloride. When dissolved in water, it dissociates into benzoquinone and nitroanilic acid; alkalis decompose it, yielding the quinone and an alkali nitroanilate, sodium ethoxide in alcoholic solution giving rise to the sodium salt.

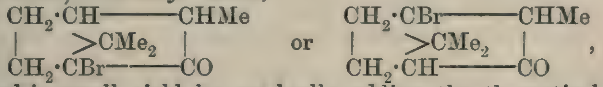
A mixture of benzoquinone and liquid nitrogen trioxide after remaining for 24 hours in a sealed tube at 12°, exploded with sufficient violence to completely shatter the wrought-iron sheath surrounding the experimental tube. G. T. M.

5-Acetylamino-1 : 2-naphthaquinone and the *iso*Rosindulines obtained therefrom. By FRIEDRICH KEHRMANN and A. DENK (*Ber.*, 1900, **33**, 3295—3300).—5-Amino-2-naphthol interacts with acetic anhydride at the ordinary temperature to form 5-*acetylamino*-2-*naphthol*, which crystallises from alcohol in greyish needles and melts at 213—214°. On dissolving it in dilute aqueous sodium hydroxide, adding sodium nitrite, and acidifying, the *nitroso*-derivative,

$$NHAc\cdot C_{10}H_5O\colon N\cdot OH,$$

is obtained; this crystallises from water, gives a bright green sodium salt, and on reduction with stannous chloride in 20 per cent. hydrochloric acid yields 5-*acetylamino*-1-*amino*-2-*naphthol*, which is readily oxidised by potassium dichromate and sulphuric acid to 5-*acetylamino*-1 : 2-*naphthaquinone*. This crystallises from chloroform in vermilion needles, melts at 150—160°, is easily soluble in water, and condenses at the ordinary temperature with *o*-aminodiphenylamine to form principally *iso*rosinduline No. 9 (Kehrmann and Steiner, this vol., i, 101) along with a small quantity of the isomeride No. 12 (*ibid.*, 100). W. A. D.

Bromofenchone. By LUIGI BALBIANO (*Gazzetta*, 1900, **30**, ii, 382—388).—*Bromofenchone*,

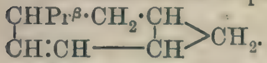


$$\begin{array}{l} CH_2\cdot CH\text{———}CHMe \\ |\quad\quad >CMe_2\quad | \\ CH_2\cdot CBr\text{———}CO \end{array} \quad \text{or} \quad \begin{array}{l} CH_2\cdot CBr\text{———}CHMe \\ |\quad\quad >CMe_2\quad | \\ CH_2\cdot CH\text{———}CO \end{array},$$

obtained in small yield by gradually adding the theoretical quantity of bromine to fenchone heated at 140—150°, is a pale yellow, oily liquid which has an aromatic, terpene-like odour and dissolves in most organic solvents; it boils undecomposed at 120° under 14 mm., and at 107° under 2 mm. pressure, has a sp. gr. 1·328 at 15°/15° and $[\alpha]_D$ − 6·8° at 9°. On reduction in alcoholic solution with zinc and sulphuric acid, it yields fenchone, but when oxidised with various oxidising reagents no definite products other than carbon dioxide, oxalic acid, and resinous acids could be obtained. T. H. P.

Terpenes and Ethereal Oils. By OTTO WALLACH (*Annalen*, 1900, **313**, 345—370. Compare Abstr., 1896, i, 101).—[With H. and E. LAUFFER.]—When purified phellandrene nitrite is treated with ammonia of sp. gr. 0·93, it is very slowly dissolved, nitrous oxide being evolved; a white solid is produced which yields nitrophellandrene when heated with water, acids, or alkalis, and this disagreement with the observations of Pesci (Abstr., 1886, 1038) is due to the fact that the material employed by that investigator was not purified sufficiently. Nitrophellandrene is also produced when phellandrene nitrite is added to acetic chloride.

Oxidation with nitric acid converts phellandrene nitrite into a neutral compound containing nitrogen, along with terephthalic and *iso*propylsuccinic acids, and an acid isomeric with the last-named substance. The *compound*, $C_7H_{10}O_4N_2$, melts at 88—89°, and gives Liebermann's reaction for nitroso-compounds; the *acid*, $C_7H_{12}O_4$, melts at 85—88°. *iso*Propylsuccinic acid is also produced when phellandrene nitrite is oxidised with potassium permanganate.

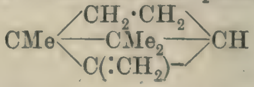
The constitution of phellandrene is best represented by the formula  $\begin{array}{l}\mathrm{CHPr^{\beta}\cdot CH_2\cdot CH}\\ \mathrm{CH{:}CH\text{——}CH}\end{array}\!>\!\mathrm{CH_2}$.

[With H. Lauffer.]—The *base*, $C_{10}H_{17}\cdot NH_2$, prepared by reducing terpinene nitrosite with sodium in alcohol, boils at 209—210°, has a sp. gr. 0·8725, and n_D 1·4717 at 20°; the carbamide derivative melts at 171°. Oxidising the corresponding alcohol converts it into the ketone, of which the *oxime* melts at 96—98°. *p*-Cymene is the non-basic reduction product of terpinene nitrosite.

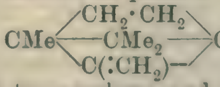
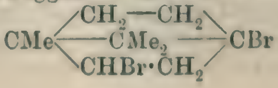
[With Alfred Schäfer.]—When *a*-pinonic acid is prepared by oxidising oil of turpentine, a peculiar, camphor-like odour is noticeable on evaporating the liquid; this is due to nopinone, the ketone obtained by oxidising nopic acid.

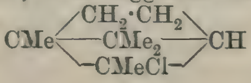
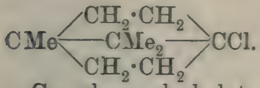
[With Wilhelm Rojahn.]—*Pinocamphylamine*, $C_{10}H_{17}\cdot NH_2$, prepared by reducing pinocamphoneoxime (Abstr., 1898, i, 486) with sodium in alcohol, is a liquid which rapidly absorbs carbon dioxide; the *carbamide* and *acetyl* derivatives melt at 204° and 120° respectively. Pinocamphonitrile (*loc. cit.*) boils at 224—226°, and is hydrolysed to *pinocampholenic acid*, $C_{10}H_{16}O_2$, which yields the amide melting at 116°.

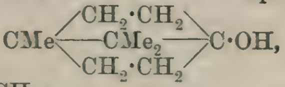
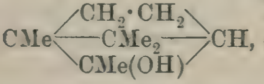
Whilst nitrosopinene yields a mixture of pinylamine and pinocamphone on reduction, the additive compound with bromine is converted into dihydrocarvone and dihydrocarvylamine. M. O. F.

Camphene. By Friedrich W. Semmler (*Ber.*, 1900, **33**, 3420—3432).—Camphene is never oxidised to camphoric acid, and probably contains a nucleus different from those of pinene and of pinene hydrochloride. The formula  $\mathrm{CMe}\left\langle\begin{array}{c}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CMe_2}\\ \mathrm{C({:}CH_2)}\end{array}\right\rangle\mathrm{CH}$ is suggested for camphene.

Pinene dibromide is reduced to a dihydrocamphene identical with that from pinene hydrochloride; it therefore contains the same nucleus as the latter, and is the product of an isomeric change similar to that which takes place in the action of hydrogen chloride on pinene.

Bromocamphene, for which the formula  $\mathrm{CMe}\left\langle\begin{array}{c}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CMe_2}\\ \mathrm{C({:}CH_2)}\end{array}\right\rangle\mathrm{CBr}$ is suggested, is reduced by sodium and alcohol to camphene, and therefore contains the camphene nucleus unchanged. Camphene dibromide is probably formed by the addition of hydrogen bromide to the bromocamphene which is the first product of the action, and is reconverted into bromocamphene by distilling with quinoline. It is not, however, readily acted on by alcoholic potash, and is reduced by sodium and alcohol to a dihydrocamphene identical with that from pinene hydrochloride; it is therefore suggested that it has the same nucleus as the latter, and the formula  $\mathrm{CMe}\left\langle\begin{array}{c}\mathrm{CH_2\text{—}CH_2}\\ \mathrm{CMe_2}\\ \mathrm{CHBr\cdot CH_2}\end{array}\right\rangle\mathrm{CBr}$ is suggested; the conversion of bromocamphene into camphenedibromide would then involve the conversion of a four-membered into a five-membered ring, as in the conversion of pinene into the hydrochloride.

Camphene hydrobromide, $C_{10}H_{16},HBr$, separates from alcohol in well-formed crystals and melts at 133°; it is reconverted into camphene by alcoholic alkalis, and also when attempts are made to reduce it with sodium and alcohol. The hydrochloride loses hydrogen chloride less readily, and gives a mixture of camphene and dihydrocamphene identical with that from pinene hydrochloride; it is suggested that the hydrochloride is perhaps a mixture of  and .

Camphene alcoholate, $C_{10}H_{17}\cdot OEt$, prepared by boiling a mixture of camphene, alcohol, and sulphuric acid, is an oil which boils at about 200°, has n_D 1·4589, a sp. gr. 0·895, and is identical with *iso*borneol ethyl ether (Bertram and Walbaum, Abstr., 1894, i, 204); this reaction does not take place with other terpenes, although nopinene and sabinene give small yields of an ether. *iso*Borneol gives a small yield of camphor when oxidised with dichromate and sulphuric acid; it may be a camphane derivative, , or a camphene derivative, , or a mixture of these.

T. M. L.

The Resin-Balsam of Picea Vulgaris, Link (Jura Turpentine). By Alexander Tschirch and Ed. Brüning (*Arch. Pharm.*, 1900, **238**, 616—630).—This turpentine was examined by the methods already described (Abstr., 1900, i, 678, &c.). From a solution of it in ether, 1 per cent. aqueous ammonium carbonate extracts *piceapimarinic acid*, $C_{13}H_{20}O_2$, an amorphous substance, which neutralises 1KOH both in the cold and on boiling. After this treatment, 1 per cent. aqueous sodium carbonate extracts a mixture of acids, from the solution of which in methyl alcohol *piceapimaric acid*, $C_{20}H_{30}O_2$, crystallises; this melts at 144—145°, and neutralises 1KOH both in the cold and on boiling; mono-*potassium*, *calcium*, *lead*, and *silver* salts were prepared. From the mother liquors of this acid, two isomeric *piceapimarolic acids*, $C_{25}H_{44}O_2$, separate; these are amorphous, and can be separated with alcoholic lead acetate, which precipitates the lead salt of the α-acid, but not that of the β-acid; the acids melt at 90—95° and 88—94° respectively; both neutralise 1KOH as well in the cold as on boiling. These resinolic acids all give the colour reactions of the cholesterols.

After removal of the acids and further washing with dilute aqueous potassium hydroxide, the ether was distilled off, and the residue distilled with steam; an *ethereal oil* came over, smelling like turpentine. There remained behind a substance of indifferent character, *juroresen*, $C_{21}H_{36}O$.

An *alkaloid* can be extracted from the turpentine with hot water. The turpentine also contains a *colouring matter*, and it yields formic, acetic, and succinic acids when distilled; no methoxyl is present.

In 100 parts of the drug there are contained: piceapimarinic acid, 2—3; piceapimaric acid, 1·5—2; α- and β-piceapimarolic acids (the former in larger amount), 48—50; ethereal oil, 32—33; juroresen, 10—12; succinic acid, colouring matter, alkaloid, water and impurities, 1—2 parts. C. F. B.

Synthesis of Luteolin. By STANISLAUS VON KOSTANECKI, A. RÓŽYCKI and JOSEF TAMBOR (*Ber.*, 1900, **33**, 3410—3417).—When 2 : 4 : 6-trimethoxyacetophenone and ethyl piperonylate dissolved in xylene are heated with sodium for 10—12 hours at 120°, condensation ensues with the formation of 2 : 4 : 6 *trimethoxybenzoyl*-3′ : 4′-*methylenedioxyacetophenone*, $C_6H_2(OMe)_3\cdot CO\cdot CH_2\cdot CO\cdot C_6H_3\colon O_2\colon CH_2$, which crystallises in small, yellow needles, melts at 115° and when warmed with hydriodic acid yields 5 : 7-*dimethoxy*-3′ : 4′-*methylenedioxyflavone*, which crystallises in clusters of silky, white needles, melts at 232°, and forms fluorescent solutions.

As this compound is not easily converted into tetrahydroxyflavone, 2 : 4 : 6 : 3′ : 4′-*pentamethoxybenzoylacetophenone* was prepared by the condensation of 2 : 4 : 6-trimethoxyacetophenone with ethyl veratrate; this is precipitated by carbon dioxide from its solution in sodium hydroxide as a white, curdy precipitate and, when treated with strong hydriodic acid, yields luteolin. R. H. P.

Hydrolysis of Solanin. By FERDINAND SCHULZ (*Zeit. Zuck.-Ind. Böhm.*, 1900, **25**, 89—94).—On hydrolysis, solanin yields about 47·52 per cent. of its weight of solanidin and 42·41 per cent. of sugar (calculated as dextrose), the latter being a mixture of dextrose with a methylpentose, probably rhamnose. T. H. P.

Oxidation of Aloin with Potassium Persulphate and with Caro's Acid. By EUGEN SEEL (*Ber.*, 1900, **33**, 3212—3214).—By the action of an excess of potassium persulphate on aloin, a red substance is produced, perhaps identical with Schaer's 'aloin red' (Abstr., 1900, i, 512). Caro's reagent gives a *tetrahydroxymethylanthraquinone*, $C_{15}H_{10}O_6$, which is perhaps identical with Oesterle's 'alochrysin' (Abstr., 1899, i, 538). T. M. L.

Crystalline Compounds in Galanga Root. By GIUSEPPE TESTONI (*Gazzetta*, 1900, **30**, ii, 327—339).—Alpinin, $C_{17}H_{12}O_6$, which Jahns (Abstr., 1882, 866) isolated, together with campheride and galangin, from galanga root (*Alpinia officinarum*), is shown by the author to be a mixture of the two last-named compounds.

The *methyl* derivative of galangin, $C_{16}H_{12}O_5$, is also present in galanga root and crystallises from methyl alcohol in pale yellow, square plates melting at about 300°. It dissolves in concentrated sulphuric acid, forming a deep yellow liquid which in a short time assumes a green fluorescence; it is also soluble in concentrated potassium hydroxide solution, giving an intense yellow colour, whilst with sodium hydroxide the corresponding salt is precipitated in minute yellow needles. Its *diacetyl* compound, $C_{20}H_{16}O_7$, separates from alcohol in faintly yellow leaflets melting at 175—176° and forms a *dibromide*, $C_{20}H_{16}O_7Br_2$, crystallising from acetic acid in yellow needles melting at 202°. The methyl derivative is transformed into galangin by hydriodic acid.

Jahns (*loc. cit.*) and Gordin (*Diss.*) prepared diacetyl- and dibenzoyl-derivatives of campheride, but the author has obtained trisubstituted derivatives, thus confirming the constitution given by von Kostanecki (Abstr., 1896, i, 44). *Triacetylcampheride*, $C_{16}H_9O_6Ac_3$, separates from alcohol in almost white needles melting at 193—194° and the *tribenzoyl* compound crystallises from acetic acid in white, mammillary masses melting at 177—178°.

On methylating campheride with methyl iodide and alcoholic potash, it yields mainly a *trimethyl* derivative, $C_{19}H_{20}O_6$, separating from methyl alcohol in square or rectangular yellow plates melting at 178°, whilst ethylation yields a *diethyl* derivative, $C_{20}H_{20}O_6$, crystallising from methyl alcohol in slender, yellow needles melting at 137—139° and a *triethyl* compound, $C_{22}H_{24}O_6$, separating from light petroleum in long, yellow needles melting at 125—126°. In these trisubstituted derivatives, one of the alkyl groups enters the nucleus of the molecule and is not present in the form of a methoxy- or ethoxy-residue.

T. H. P.

Tiliadin, a Constituent of the Bark of Lime Trees. By WALTER BRAEUTIGAM (*Arch. Pharm.*, 1900, **238**, 555—567).—When the bark of the lime tree is extracted with ether, the extract evaporated, and the residue washed thoroughly with 90 per cent. alcohol, the alcohol extracts a little vanillin. If the residue is boiled with 5 per cent. aqueous potash and then dissolved in ether, the solution deposits crystalline plates as it evaporates; this substance, *tiliadin*, $C_{21}H_{32}O_2$, melts at 228—229°, volatilises when heated cautiously, and is dextrorotatory in chloroform solution. In many of its reactions it resembles the cholesterols, but in others it differs from them; it has not the properties of a glucoside. It does not lose water of crystallisation when heated at 125°, nor will it form acetyl or benzoyl derivatives. Strong hydrochloric acid is without effect on it, even at 160°. Boiling with aqueous alkali hydroxides is without effect; on the other hand, alcoholic potash at 150° converts it into a *substance*, $C_{13}H_{18}O$, which crystallises in needles, begins to melt at 179—180°, and volatilises when heated cautiously. Fusion with potassium hydroxide converts tiliadin into resinous products, but oxalic acid is not formed. Boiling with nitric acid has no effect, but at 160° a resinous product is obtained. Potassium permanganate does not oxidise it in cold acetic acid solution, but it does on boiling, and so does chromic acid; the product is a resinous substance, with the composition $C_{21}H_{32}O_4$. When treated with chlorine or bromine in chloroform solution, tiliadin yields products containing chlorine and bromine; with iodine, no similar product could be obtained.

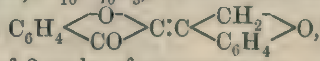
On the west side of the tree, the bark frequently has a green coating of an alga, *Pleurococcus vulgaris*; from this a *substance* crystallising in needles was obtained; these crystallise out along with the plates of tiliadin in the preparation of the latter, if the bark has not been freed from the green coating. C. F. B.

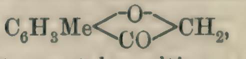
Blue Chlorophyllin. By M. Tsvett (*Compt. rend.*, 1900, **131**, 842—844).—The blue chlorophyllin was isolated from the plants by a method which is described in detail. It was obtained in a microcrystalline state, the crystals having a black colour and a bluish lustre. The absorption spectrum of its solution consists of six bands, the fourth band being situated near the Fraunhofer line E, and the fifth commences at the line F. H. R. Le S.

Composition of the Orange Pigment of Uraster Rubens. By Arthur Bower Griffiths and F. W. Warren (*Bull. Soc. Chim.*, 1900, [iii], **23**, 874—875).—The orange pigment extracted from the skin of *Uraster rubens* has the composition $C_{16}H_{18}O_2N_4$; its solutions do not show characteristic absorption bands. N. L.

Syntheses of Coumaranone (Ketocoumaran) and its Homologues from Phenoxyacetic Acid. By Richard Stoermer and F. Bartsch (*Ber.*, 1900, **33**, 3175—3181. Compare Abstr., 1899, i, 675).—Coumaranone is most easily obtained by the dehydration of phenoxyacetic acid suspended in benzene with phosphoric oxide, and is separated from the unaltered acid by distillation with steam; when pure, it is quite stable and has a pleasant odour of hyacinths. It sublimes at the ordinary temperature in long, slender needles and melts at 101—102°. The *semicarbazone*, $C_9H_9O_2N_3$, separates from alcohol in yellowish crystals and melts at 231°. The *oxime*, $C_8H_7O_2N$, crystallises from hot dilute alcohol and melts at 159°.

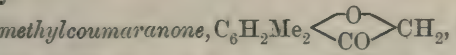
1-o-*Hydroxybenzylidenecoumaranone*, $C_{15}H_{10}O_3$, separates from hot dilute alcohol in slender, yellowish crystals melting and decomposing at 208°; it dissolves in alkalis with an intense red colour. 1-p-*Hydroxybenzylidenecoumaranone* is a greenish-yellow, crystalline substance which melts and decomposes at 242°. The two foregoing compounds are substantive dyes.

During the preparation of coumaranone, a considerable quantity of a reddish-brown *substance*, $C_{16}H_{10}O_3$, is obtained as a bye-product. This has the constitution  $C_6H_4{<}\substack{-O-\\CO}{>}C{:}C{<}\substack{CH_2\\C_6H_4}{>}O$, and is probably formed by condensation of 2 mols. of coumaranone.

6-*Methylcoumaranone*,  $C_6H_3Me{<}\substack{-O-\\CO}{>}CH_2$, from o-tolyloxyacetic acid, forms yellowish-white crystals melting at 102°, is volatile with steam, and dissolves readily in the common organic solvents or in hot water. With Fehling's solution, it yields a red dye similar to that obtained from coumaranone. The *semicarbazone*, $C_{10}H_{11}O_2N_3$, separates from hot dilute alcohol in yellowish crystals melting at 229°. The *oxime*, $C_9H_9O_2N$, is yellow, dissolves in ether, benzene, or alcohol, and melts at 148°. 1-o-*Hydroxybenzylidene*-6-*methylcoumaranone*, $C_{16}H_{12}O_3$, crystallises from hot alcohol in yellow needles, dissolves in alkalis, yielding an intense red solution and sublimes and decomposes at 196°. The corresponding *para*-compound forms yellow leaflets which decompose at 210—215°.

5-*Methylcoumaranone*, $C_9H_8O_2$, unlike the analogous substances already described, is an oil, and boils at 106—112° under 15 mm. pressure; its properties closely resemble those of coumaranone. The *semicarbazone*, $C_{10}H_{11}O_2N_3$, is yellowish and melts at 208°, the *oxime* $C_9H_9O_2N$, is yellow and melts at 151°. The o- and p-*hydroxybenzylidene* derivatives, $C_{16}H_{12}O_3$, are yellowish-brown, the former decomposes at 192°, the latter at 212°.

4-*Methylcoumaranone*, $C_9H_8O_2$, is a yellowish liquid which boils without decomposition in a vacuum. The *semicarbazone*, $C_{10}H_{11}O_2N_3$, melts at 181°, and the *oxime*, $C_9H_9O_2N$, at 144°. The o- and p-*hydroxybenzylidene* derivatives, $C_{16}H_{12}O_3$, decompose at 210° and 163° respectively.



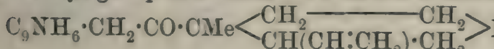
4:6-*Dimethylcoumaranone*, $C_6H_2Me_2{<}\substack{O\\CO}{>}CH_2$, from *as*-*m*-xylyloxyacetic acid, melts at 142°. Its *oxime*, $C_{10}H_{11}O_2N$, melts at 148°.

A. L.

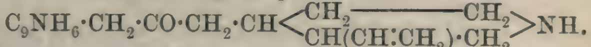
The Cinchona Alkaloids. By WILHELM VON MILLER and GEORG ROHDE [in part with JOSEF BRUNNER and ERNST FUSSENEGGER] (*Ber.*, 1900, **33**, 3214—3237).—The identity of Pasteur's cinchonicine and quinicine (*Jahresber. der Chem.*, 1853, 473) with cinchotoxine and quinotoxine has been established.

By the action of amyl nitrite and sodium ethoxide cinchotoxine is converted into an iso*nitroso*-derivative, $C_{19}H_{21}O_2N_3$, which separates in crystal aggregates from chloroform when ether is added, melts at 169—170°, and, like other secondary piperidine bases, gives a purple coloration with nitrobenzene containing nitrothiophen; the salts do not give this reaction. The *hydrochloride*, $C_{19}H_{21}O_2N_3,HCl$, melts at 268°, crystallises from alcohol or hot water in prismatic plates, dissolves in acids and alkalis, and gives Liebermann's reaction; the *acetate* melts at 200°, and the *sulphate*, *nitrate*, *formate*, and *phosphate* are also crystalline. The *methiodide*, $C_{19}H_{21}O_2N_3,MeI$, crystallises from methyl alcohol in prisms and plates, melts at 235°, and, unlike most secondary bases, is not acted on by aqueous alkalis; when treated with sodium ethoxide, it gives a base identical with the *iso*nitroso-derivative of methylcinchonine, and it would therefore appear that in the removal of hydrogen iodide from the methiodide the cinchotoxine is reconverted into a cinchonine derivative.

By the action of an excess of amyl nitrite on cinchotoxine, Miller and Rohde's nitroso*iso*nitrosocinchotoxine (Abstr., 1895, i, 433) is produced, and not a di*iso*nitroso-derivative; it would therefore appear that cinchotoxine contains only one methylene group adjacent to a carboxyl group in accordance with the formula



$C_9NH_6{\cdot}CH_2{\cdot}CO{\cdot}CMe{<}\substack{CH_2\text{————}CH_2\\CH(CH{:}CH_2){\cdot}CH_2}{>}NH$, and not



$C_9NH_6{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH{<}\substack{CH_2\text{————}CH_2\\CH(CH{:}CH_2){\cdot}CH_2}{>}NH.$

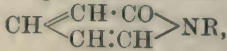
The action of *p*-bromophenylhydrazine on quinotoxine gave a mixture of substances, one of which crystallised in yellow aggregates melting at 141° and proved to be a p-*bromophenylhydrazone*, $C_{26}H_{29}ON_4Br$; a second product crystallising in minute yellow needles and melting 15—20° higher is perhaps the geometrical isomeride.

Nitrosoquinotoxine, $C_{20}H_{23}O_3N_3$, prepared by the action of nitrous acid on quinotoxine, crystallises from a mixture of acetone or benzene with light petroleum in colourless needles, melts at 94°, dissolves in acids and gives Liebermann's reaction; the *phenylhydrazone*, $C_{26}H_{29}O_3N_5$, crystallises from alcohol and melts at 140°. *Nitroso*iso*nitrosoquinotoxine*, $C_{20}H_{22}O_4N_4$, which is also produced in the action of nitrous acid on quinotoxine, crystallises from alcohol in large, colourless prisms, melts at 186°, and dissolves in alkalis to a yellow solution.

The action of methyl iodide on quinotoxine is similar to its action on cinchotoxine, the products being methylquinine (Claus and Mallmann, Abstr., 1881, 619) and its methiodide; the anhydrous methiodide melts at 180°, not at 215—218°.

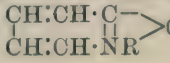
iso*Nitrosoquinotoxine*, $C_{20}H_{23}O_3N_3$, crystallises from a mixture of alcohol and benzene in yellowish aggregates, melts at 168—170°, and gives the nitrothiopen reaction. The *hydrochloride*, $C_{20}H_{20}O_3N_3,HCl$, crystallises from alcohol in large tablets and melts at 244°; the *acetate*, *sulphate*, and *nitrate* are crystalline and do not give the nitrothiophen reaction. The *methiodide*, $C_{21}H_{26}O_3N_3I$, crystallises from methyl alcohol, melts at 175°, and is not acted on by aqueous alkalis. By the action of sodium ethoxide the quinine complex is reproduced, the product being an iso*nitrosomethylquinine*, which separates as a yellow, amorphous base, melts at 90—100°, and is identical with the base prepared from amyl nitrite and methylquinine; the identity of the bases was also proved by conversion into the *methiodide*, $C_{22}H_{28}O_3N_3I$, melting at 169—170°, and the *nitrate* melting at 175°. T. M. L.

Constitution of Pyridones, Quinolones, and Analogous Bases. By HERMANN DECKER (*J. pr. Chem.*, 1900, [ii], **62**, 266—270).—A discussion of the formulæ of pyridones and analogous bases. The author favours formulæ of the ketonic type,



$\mathrm{CH}<\begin{matrix}\mathrm{CH\cdot CO}\\ \mathrm{CH{:}CH}\end{matrix}>\mathrm{NR}$,

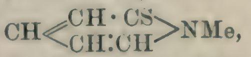
which he considers represent the reactions of these bases better than formulæ of the type



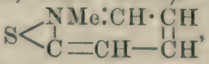
$\begin{matrix}\mathrm{CH{:}CH\cdot C}-\\ |\qquad\quad \| \\ \mathrm{CH{:}CH\cdot NR}\end{matrix}>\mathrm{O}$,

which contain quinquevalent nitrogen. R. H. P.

Thio-1-methylpyridone and Thio-1-methylquinolone. By ALEXANDER GUTBIER (*Ber.*, 1900, **33**, 3358—3359).—*Thio-1-methylpyridone*,



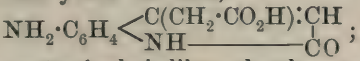
$\mathrm{CH}<\begin{matrix}\mathrm{CH\cdot CS}\\ \mathrm{CH{:}CH}\end{matrix}>\mathrm{NMe}$, or



$\mathrm{S}<\begin{matrix}\mathrm{NMe{:}CH\cdot CH}\\ |\qquad\qquad\ \| \\ \mathrm{C=CH-CH}\end{matrix}$,

obtained by heating 1-methylpyridone with phosphorus pentasulphide for 4—5 hours at 130°, crystallises from hot water in yellowish-white leaflets, melts at 89—90°, and distils unchanged; it is feebly basic, dissolving in concentrated sulphuric or hydrochloric acid. *Thio-1-methylquinolone*, obtained similarly, forms long, pointed, yellowish-green prisms, melts at 118°, boils unchanged above 370°, and resembles the foregoing thiopyridone. Both substances, like 1-methylpyridone and 1-methylquinolone from which they are derived, fail to interact with hydroxylamine in either neutral or alkaline solution. W. A. D.

Action of Ethyl Acetonedicarboxylate on *m*-Phenylenediamine. By EMIL BESTHORN and E. GARBEN (*Ber.*, 1900, **33**, 3448—3453. Compare Abstr., 1898, i, 450).—*Ethyl 7-amino-2-quinolone-4-acetate* is obtained when molecular quantities of ethyl acetonedicarboxylate and *m*-phenylenediamine are heated together for several hours in sealed tubes at 100°; on hydrolysis with hydrochloric acid, it yields *7-amino-2-quinolone-4-acetic acid* in the form of its *hydrochloride* which when washed with water yields the *acid*,



$$\mathrm{NH_2\cdot C_6H_4}<\begin{array}{l}\mathrm{C(CH_2\cdot CO_2H):CH}\\ \mathrm{NH}\text{————————}\mathrm{CO}\end{array};$$

this crystallises from water in hair-like, colourless needles melting at about 271°, is only sparingly soluble in the usual organic solvents, and its solution exhibits a blue fluorescence. The *calcium* salt contains $5H_2O$, the *ethyl* ester crystallises in needles melting at 197—198°, is sparingly soluble and its solutions also fluoresce. When the acid is rapidly heated at 300°, it loses carbon dioxide and yields 7-aminolepidone (7-amino-2-hydroxylepidine); when treated with nitrous acid, it yields *7-hydroxy-2-quinolone-4-acetic acid*, which crystallises from hot water in felted needles melting at about 320°; it forms a *hydrochloride* which is decomposed by water, and an *ethyl* ester crystallising in minute needles and melting at 204—205°, but after solidification at above 220°. When the acid is carefully heated, it yields 7-hydroxylepidone (2 : 7-dihydroxylepidine). J. J. S.

Stereoisomeric Schiff's Bases. By ALEXANDER EIBNER and FRZ. PELTZER (*Ber.*, 1900, **33**, 3460—3469. Compare Abstr., 1894, i, 410).—When aqueous solutions of *o*-toluidine and acetaldehyde are mixed and kept at the ordinary temperature for 24 hours, an *ethylidene-o-toluidine*, $C_{18}H_{22}N_2$, crystallising in small needles and melting, after repeated recrystallisation from alcohol, at 90—92° is obtained; it dissolves readily in both dilute and strong hydrochloric acid, but yields a sparingly soluble *nitrate*; when benzoylated by the Schotten Baumann method, it yields a *benzoyl* derivative, $C_{25}H_{26}ON_2$, melting at 179°, together with a small amount of the isomeric benzoyl compound melting at 230°. Its *dinitroso*-derivative, $C_{18}H_{20}O_2N_4$, crystallises in yellow needles melting at 130° and is sparingly soluble in alcohol; when reduced, it yields *p*-phenylenediamine and 2 : 8-dimethyltetrahydroquinoline. When the base is distilled, it yields 2 : 8-dimethylquinoline together with a small amount of the isomeric base melting at 116°.

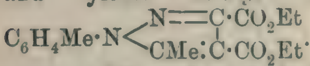
If the solution of acetaldehyde and *o*-toluidine is warmed, shaken, or kept at the ordinary temperature for several weeks, an *ethylidene-o-toluidine* melting at 116° is obtained; this crystallises in small prisms or plates, is readily soluble in most solvents with the exception of light petroleum, forms a *hydrochloride*, a sparingly soluble *nitrate* melting at 155°, a *diacetyl* derivative melting at 155°, a *dinitroso*-compound melting at 155°, and a *benzoyl* derivative melting at 230°; the latter forms a *nitroso*-compound melting at 190° The base itself can be distilled without undergoing any great decomposition and is not reduced when treated with sodium and amyl alcohol. The same base is obtained when the isomeride of low melting point is heated for 4 hours at 120—125°, or when its ethereal solution is treated with iodine. When the condensation takes place in acetic or hydrochloric acid solution, the compound melting at 116° is alone formed. J. J. S.

Action of Nitrosobenzene on Aromatic Hydrazines. By OSKAR SPITZER (*Chem. Centr.*, 1900, ii, 1108; from *Oesterr. Chem. Zeit.*, **3**, 489—490).—Whilst by the action of nitrosobenzene on hydrazobenzene, azobenzene and water only are formed, with phenylhydrazine, nitrosobenzene yields, not only these products, but also nitrogen and benzene. The latter reaction may be used to estimate the quantity of nitrogen present as nitroso-groups in organic compounds. E. W. W.

Phenylmethylpyrazolecarboxylic Acids. By CARL BÜLOW (*Ber.*, 1900, **33**, 3266—3270).—The acid formerly described by Bülow and Schlesinger as 1-phenyl-3-methyl*iso*pyrazole-4 : 5-dicarboxylic acid (Abstr., 1900, i, 36) is in reality 1-*phenyl-5-methylpyrazole*-3 : 4-*dicarboxylic acid* (compare Stolz, Abstr., 1900, i, 252); it is produced, together with Knorr and Laubmann's dicarboxylic acid (Abstr., 1889, 409), by oxidising 1-phenyl-3 : 5-dimethylpyrazole-4-carboxylic acid with potassium permanganate; it is identical with the substance produced from diethyl benzeneazodiacetylsuccinate, and yields, by the successive elimination of its carboxyl groups, 1-phenyl-5-methylpyrazole-4-carboxylic acid (m. p. 166°) and 1-phenyl-5-methylpyrazole.

The isomeric acid described by Knorr and Laubmann as melting at 198° has a melting point 203—204°, and is 1-phenyl-3-methylpyrazole-4 : 5-dicarboxylic acid; it yields 1-phenyl-3-methylpyrazole-4-carboxylic acid (m. p. 192·5—193°) and 1-phenyl-3-methylpyrazole by the successive removal of carboxyl. G. T. M.

Preparation of Pyrazole Derivatives from Azo-compounds of Diacetosuccinic Esters. By CARL BÜLOW and ALFRED SCHLESINGER (*Ber.*, 1900, **33**, 3362—3369).—The following facts form an extension of a previous paper (preceding abstract). *Diethyl* p-*tolueneazodiacetosuccinate*, $C_6H_4Me\cdot N_2\cdot CAc(CO_2Et)\cdot C(CO_2Et)\colon CMe\cdot OH$, obtained by combining *p*-toluenediazonium chloride with ethyl diacetosuccinate, separates from alcohol in yellow crystals, melts at 119—120°, and on boiling with water for 8 hours loses acetic acid (1 mol.), and yields *diethyl* 1-p-*tolyl-5-methylpyrazole*-3 : 4-*dicarboxylate*,



$$C_6H_4Me\cdot N<\begin{matrix}N{=\!=}C\cdot CO_2Et\\ CMe{:}C\cdot CO_2Et\end{matrix}$$

This crystallises from dilute alcohol, melts at 50°, and on hydrolysis with dilute mineral acids or alkalis yields 1-p-*tolyl-5-methylpyrazole*-3 : 4-*dicarboxylic acid*, which forms slender needles, melts at 246°, and yields an acid *silver* salt, $C_{13}H_{11}O_4N_2Ag$, as a white powder, insensitive to light. On heating the acid above its melting point, it loses carbon dioxide and yields a mixture of 1-p-*tolyl-5-methylpyrazole* and its 4-*carboxylic acid*. The former is a yellowish oil, which boils at 270—280°, is volatile in steam, and yields a crystalline platinichloride melting and decomposing at 214°; its 4-carboxylic acid is crystalline, and melts at 199—200°.

Diethyl β-naphthaleneazodiacetosuccinate, prepared from diazotised *β*-naphthylamine and diethyl acetosuccinate at 0°, separates from dilute alcohol in reddish-yellow crystals and melts at 108°. *Diethyl*

1-*β-naphthyl-5-methylpyrazole*-3 : 4-*dicarboxylate* crystallises from dilute alcohol in nearly colourless, lustrous leaflets and melts at 82° ; the corresponding *dicarboxylic acid* melts at 250°, and on dissolving in ammonia and adding silver nitrate, yields the *silver* salt, $C_{16}H_{11}O_4N_2Ag$, as a heavy, white precipitate. 1-*β-Naphthyl-5-methylpyrazole* melts at 65°, boils at 320—330°, and yields a crystalline *platinichloride* melting at 217°. W. A. D.

Theories of Dyeing. By PAUL SISLEY (*Bull. Soc. Chim.*, 1900, [iii], **23**, 865—874).—In this paper, the researches of Witt, Knecht, von Georgevics, and Gillet are briefly reviewed, and a description is then given of some fresh experiments favouring Witt's dissolution theory, according to which the dyeing of a fibre is analogous to the extraction of a colouring matter from its aqueous solution by means of an immiscible solvent.

When pure, colourless rosaniline is boiled with water, a coloured solution is obtained which quickly dyes silk ; in the presence of excess of alkali (1·5 grams of sodium hydroxide per litre) no coloration is produced. According to Knecht, when silk is dyed with magenta in neutral solution, the exhausted liquid contains the whole of the hydrogen chloride of the dye as ammonium chloride. The author confirms the presence of hydrogen chloride, to some extent, at least, but no ammonia could be detected in the bath. When 100 c.c. of water are boiled with 2 c.c. of normal sodium hydroxide and a little rosaniline, a colourless solution is obtained which dyes silk and yields a red colour to amyl alcohol when boiled therewith. Malachite-green, crystal-violet, and Victoria-blue behave in a similar way ; aniline may be used instead of amyl alcohol. These results are shown to be due neither to impurities in the substances employed nor to the action of carbon dioxide. Their explanation is rather to be sought in von Georgevics' hypothesis, according to which the silk, amyl alcohol, or aniline bring about the molecular transformation of the colourless base $OH{\cdot}C(C_6H_4{\cdot}NH_2)_3$ into a coloured isomeride,

$$OH{\cdot}NH_2{:}C_6H_4{:}C(C_6H_4{\cdot}NH_2)_2.$$

The latter does not form a coloured salt with the substance of the fibre, as required by the purely chemical theory of dyeing, but forms either a solid solution with the fibre or a liquid solution with the amyl alcohol or aniline. This view is confirmed by the observations of Hantzsch on colourless and coloured modifications of triphenylmethane derivatives. Moreover, when silk dyed with rosaniline is boiled with alcohol, the colouring matter is readily dissolved, whilst the fibre does not lose in weight. According to the chemical theory, the alcoholic extract should either be colourless or, if coloured, should contain a portion of the acid substances of the fibre in solution. The fact that in acid solutions animal fibres are dyed with the colour of the alkali salt has been adduced as an argument in favour of the chemical theory of dyeing, the fibre being here held to play the part of a base. It is now shown, however, that amyl alcohol behaves in precisely the same manner as silk in this respect, so that the facts are really in accord with the dissolution theory. Certain facts, however, appear to contradict Witt's view that a colouring matter, in order to be fast, must necessarily be more soluble in the substance of the fibre than in water. Thus, when silk is dyed with a very dilute solution of a colouring matter, the whole of the latter is extracted from the liquid by the fibre, whereas when a large amount of the dye is used only a comparatively small proportion of it is taken up by the silk. The relative solubilities of the dye in the fibre and in water seem, in fact, to vary greatly with the concentration. Nevertheless, it is believed that experiments now in progress will show that in many cases the behaviour of immiscible solvents is in this respect also identical with that of animal fibres. N. L.

Coloured Rosaniline Bases. By Hugo Weil (*Ber.*, 1900, **33**, 3141—3144).—In reply to von Georgievics (Abstr., 1900, i, 569), the author adheres to his previous statments (Abstr., 1896, i, 565):

1. That the red precipitate obtained by von Georgevics is really a mixture of rosaniline with a small amount of its hydrochloride.

2. That when a solution of rosaniline carbonate is "salted out" with pure sodium chloride the solution becomes colourless and the clear liquid after concentration gives a blue colour with litmus.

J. J. S.

Relation between the Chemical Constitution of Triphenylmethane Colouring Matters and the Absorption Spectra of their Aqueous Solutions. By Paul Lemoult (*Compt. rend.*, 1900, **131**, 839—842).—Aqueous solutions of dyes of the triphenylmethane series in all cases give an absorption spectrum which contains a characteristic band of unabsorbed light in the red. The position of the centre of this red space is constant for those dyes which contain two tertiary nitrogen atoms and also for those containing three tertiary nitrogen atoms, but its position in the latter case is quite distinct from that in the former. The solutions employed had a thickness of 6 mm., and contained a gram-mol. of the substance in 1000 litres.

H. R. Le S.

Relation between the Chemical Constitution of the Triphenylmethane Colouring Matters and their Absorption Spectra in Aqueous Solution. By Charles Camichel (*Compt. rend.*, 1900, **131**, 1001—1002).—The observation made by Lemoult (preceding abstract) relating to the presence of fixed red bands of unabsorbed light in the spectra of triphenylmethane colouring matters containing two or three tertiary nitrogen atoms in the para-position with reference to the methane carbon atom, is only a special case of the law enunciated by Bayrac and the author (Abstr., 1896, ii, 346), who found it to hold for a series of indophenols dissolved in water and other solvents.

The ethereal solution of an indophenol may be advantageously employed as a monochromatic screen instead of red glass.

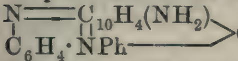
G. T. M.

The Twelfth Isomeride of Rosinduline. By Friedrich Kehrmann and G. Steiner (*Ber.*, 1900, **33**, 3276—3279. Compare Abstr., 1900, i, 463).—Phenyl*iso*naphthaphenazonium nitrate (Abstr., 1898, i, 154), when left with fuming nitric acid for 24 hours at 0°, yields a mixture of 2-*nitro*- and 4-*nitro*-12-*phenyl*iso*naphthaphenazonium nitrates*. The former, although sparingly soluble in absolute alcohol, crystallises from dilute alcohol in lustrous, yellow needles, and on reduction yields *iso*rosinduline No. 10 (Abstr., 1900, i, 463), a fact which determines its structure; the latter is easily soluble in alcohol and could not be obtained pure, although the corresponding iso*rosinduline* (No 12) [4-*amino*-12-*phenyl*iso*naphthaphenazonium*], formed on reduction, was readily isolated, by taking advantage of the slight solubility of its *bromide* in saturated aqueous sodium bromide. The salt crystallises in well-formed, nearly black prisms, with a bluish surface-colour; the *dichromate* is a dark green, microcrystalline powder.

4-*Acetylamino*-12-*phenyl*iso*naphthaphenazonium* 12-*bromide* is very soluble in water, and cannot be separated by saturating the solution with sodium bromide; the *chloride*, however, crystallises on adding sodium chloride in thick, reddish-brown, prisms or plates, whilst the *platinichloride* forms dark red, granular crystals.

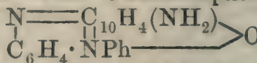
The structure of the *iso*rosinduline No. 12 follows from its synthesis from 5-acetylamino-1:2-naphthaquinone (Kehrmann and Denk, this vol., i, 89). W. A. D.

Constitution of *iso*Rosinduline No 9. By FRIEDRICH KEHRMANN and G. STEINER (*Ber.*, 1900, 33, 3280—3284).

—Details are given for preparing 2:5-diamino-1:4-naphthaquinoneimide hydrochloride (compare Kehrmann and Haberkant, Abstr., 1899, i, 62) from Ekstrand's naphthapicric acid (2:4:5-trinitro-α-naphthol), the structure of which has recently been determined (Graebe, Abstr., 1900, i, 24; Friedländer, *ibid.*, 150); the salt is much more stable than hitherto thought, not being changed by boiling water. The diamino-α-naphthaquinone and aminohydroxy-α-naphthaquinone derived from it by the action of alkalis have the structures $[O_2:(NH_2)_2 = 1:4:2:5]$ and $[O_2:NH_2:OH = 1:4:5:2]$ instead of those originally given (Abstr., 1899, i, 62). The 5-amino-2-hydroxy-1:4-naphthaquinone is best prepared by heating the hydrochloride in aqueous solution with dilute sulphuric acid; it does not condense with phenyl-*o*-phenylenediamine in alcoholic or glacial acetic acid solution, but in 80 per cent. acetic acid solution at 100° it yields 4-*aminorosindone*,  $\left.\begin{array}{l} N{=\!=}C_{10}H_4(NH_2) \\ | \qquad \| \\ C_6H_4\cdot NPh \end{array}\right> O$, which was isolated in the form of its *acetyl* derivative. This crystallises from alcohol in golden needles, melts at 280°, and shows a red fluorescence in alcoholic solution; on warming with dilute sulphuric acid, it yields pure 4-aminorosindone, which crystallises from alcohol in bronze coloured leaflets, melts at 253°, and can also be obtained by the action of cold alcoholic sodium hydroxide on *iso*rosinduline No. 9 (Kehrmann and Filatoff, Abstr., 1900, i, 60). This latter fact, together with the work of Kehrmann and Denk (this vol., i, 89), show that *iso*rosinduline No. 9 is a 4-*amino*-7-*phenylnaphthaphenazonium*. W. A. D.

Constitution of the Naphthapicric Acid melting at 145°. By FRIEDRICH KEHRMANN and G. STEINER (*Ber.*, 1900, 33, 3285—3291).

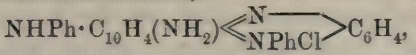
—The trinitro-α-naphthol (naphthapicric acid) melting at 145°

(Kehrmann and Haberkant, Abstr., 1899, i, 62) can be readily separated from its isomeride melting at 190°, on account of the sparing solubility in water of its *sodium* salt, which crystallises in slender, sulphur-yellow needles; the following facts show that it has the constitution [$OH:(NO_2)_3=1:2:4:7$], and the substance formerly described (*loc. cit.*) as 2:6-diamino-1:4-naphthaquinoneimide is therefore a 2:7-diamino-compound. The latter, when warmed with water, yields a mixture of 2:7-*diamino*-1:4-*naphthaquinone* with 4:7-*diamino*-1:2-*naphthaquinone*, which can readily be removed by extraction with cold 10 per cent. aqueous sodium hydroxide, in the form of the sodium derivative of the tautomeric 7-*amino-2-hydroxy*-1:4-*naphthaquinoneimide.* The pure α-quinone forms small prisms which are chocolate-brown with a violet tinge in colour, sublimes and partly decomposes at 230°, yields an orange-yellow *hydrochloride,* and does not combine with ortho-diamines; the β-quinone forms blackish-violet crystals, and yields a violet solution with dilute hydrochloric acid. Both of the quinones when boiled with dilute caustic alkalis yield 7-*amino-2-hydroxy*-1:4-*naphthaquinone* along with decomposition products which render purification difficult; the substance isolated forms brownish-red crystals, and combines with *o*-aminodiphenylamine (1 mol.) to form a 2-*aminorosindone,*  $\left.\begin{array}{l}N{=\!=\!=}C_{10}H_4(NH_2)\\ |\qquad \| \\ C_6H_4\cdot NPh\end{array}\right\rangle O$, which yields an *acetyl* derivative crystallising in lustrous, red leaflets melting at 325—335°, identical with the substance formed by the oxidation in the air of an alkaline alcoholic solution of 2-acetylamino-7-phenylnaphthaphenazonium chloride (Abstr., 1900, i, 463), the latter fact determining its structure.

Confirmatory evidence as to the structure of the new naphthapicric acid is afforded by the fact that the foregoing 4:7-diamino-1:2-naphthaquinone yields with *o*-aminodiphenylamine a 2-*aminorosinduline,* identical with the substance obtained by acting on 2-acetamino-7-phenylnaphthaphenazonium chloride (Abstr., 1900, i, 463) with alcoholic ammonia, and subsequently eliminating the acetyl group; the *chloride* forms slender, violet-brown needles, the *acetyl* derivative, $C_{24}H_{19}ON_4Cl$, crystallises from alcohol in dark-red needles with a brownish sheen, whilst the *dichromate,* $(C_{24}H_{19}ON_4)_2Cr_2O_7$, is a red powder.
W. A. D.

The Thirteenth Isomeride of Rosinduline. By FRIEDRICH KEHRMANN and M. SILBERSTEIN (*Ber.*, 1900, 33, 3300—3307. Compare preceding abstracts).—4-Anilino-6-acetylamino-1:2-naphthaquinone (Kehrmann and Matis, Abstr., 1899, i, 81) condenses with *o*-aminodiphenylamine hydrochloride in boiling dilute acetic acid solution to form principally 3-*acetylaminophenylrosinduline chloride* (3-*acetylamino-5-anilino-7-phenylnaphthaphenazonium chloride*), along with a small quantity of the isomeric 12-*phenyl*iso*naphthaphenazonium chloride*; the latter separates first in brownish-red needles, and will be described in a later communication, whilst the former is obtained only on salting out. It crystallises from alcohol in thick, dark-red prisms with a golden sheen, and with dilute alcoholic sodium hydroxide yields the *base,* $C_{30}H_{23}ON_4\cdot OH$, in brownish-red leaflets with a bronze-like lustre.

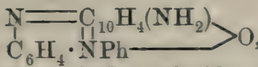
3-Aminophenylrosinduline chloride,



$$NHPh\cdot C_{10}H_4(NH_2)<\begin{matrix}N\text{——}\\ NPhCl\end{matrix}>C_6H_4,$$

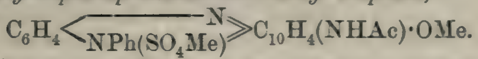
separates on boiling the acetyl derivative with alcoholic hydrochloric acid, in thick crystals with a greenish lustre; from solutions containing an excess of hydrochloric acid, the *hydrochloride*, $C_{28}H_{22}N_4Cl_2$, is obtained.

3-Aminorosindone,



$$\begin{matrix}N=\!=\!=C_{10}H_4(NH_2)\\ | \qquad || \\ C_6H_4\cdot NPh\text{————}\end{matrix}>O,$$

is formed on heating 3-acetylamino-7-phenylrosinduline chloride with 10 per cent. sulphuric acid for 2—3 hours at 175—180°; the *acetyl* derivative crystallises from acetic anhydride in vermilion-red needles with a greenish, metallic lustre, does not melt or decompose at 310°, and unites with methyl sulphate in nitrobenzene solution at 150° to form *3-acetylamino-5-methoxy-7-phenylnaphthaphenazonium methyl sulphate,*



$$C_6H_4<\begin{matrix}\text{————}N\\ NPh(SO_4Me)\end{matrix}\geqslant C_{10}H_4(NHAc)\cdot OMe.$$

This is precipitated on adding ether as an orange, crystalline powder, which regenerates rosindone on boiling with water containing a trace of alkali, and yields a *platinichloride*, $(C_{25}H_{20}O_2N_3)_2PtCl_6$, as an orange-yellow, flocculent precipitate; on warming with alcoholic ammonia, evaporating, extracting with water, and adding sodium bromide, *3-acetylaminorosinduline bromide* separates. It crystallises from boiling alcohol in vermilion needles with a greenish lustre, and yields an insoluble microcrystalline *dichromate*, $(C_{24}H_{19}ON_4)_2Cr_2O_7$; on elimination of the amino-group by the diazo-reaction, it forms *3-acetylamino-7-phenylnaphthaphenazonium*, isolated as the *chloride* in the form of an orange powder, sparingly soluble in water, which in dilute aqueous solution yields, on adding nitric acid, microscopic red needles of the *nitrate*. iso*Rosinduline* No. 13 (*3-amino-7-phenylnaphthaphenazonium*) was obtained by heating the foregoing chloride with 50 per cent. sulphuric acid; the *bromide* forms olive-green needles and dissolves in water with a brownish-red, but in alcohol with a dark-green, coloration. It is somewhat unstable in solution, yielding aminorosindone on boiling; alcoholic ammonia converts it into aminorosinduline.

The above indirect method of obtaining *iso*rosinduline No. 13 became necessary because 6-acetylamino-1 : 2-naphthaquinone with *o*-aminodiphenylamine yields only the isomeric *iso*rosinduline No. 7 (Abstr. 1899, i, 525).

W. A. D.

Osmophoric Groups.* By HANS RUPE and KARL VON MAJEWSKI (*Ber.*, 1900, **33**, 3401—3408).—The principal "osmophoric" groups are $-OH$, $=O$, $-CHO$, $-COMe$, $-OMe$, $-NO_2$, $-CN$, $-N_3$ (triazo-). Analogous compounds containing $-CHO$, $-NO_2$, $-CN$, $-N_3$ have similar odours.

Piperonylamide, $NH_2\cdot CO\cdot C_6H_3{:}O_2{:}CH_2$, obtained by treating piperonylonitrile with hydrogen peroxide, crystallises in lustrous prisms or needles, melts at 169°, in common with piperonylonitrile has a similar odour to piperonal, and, when treated with bromine and sodium hydroxide, yields p-*aminocatechol methylene ether*, which is a white, crystalline substance, melts at 44—46°, boils at 144° under 16 mm. pressure, and forms a *hydrochloride*, and an *acetyl* derivative melting at 135°. *Triazopyrocatechol methylene ether*, $N_3 \cdot C_6H_4 \vdots O_2 \vdots CH_2$, obtained from the hydrochloride just mentioned, crystallises in yellow leaflets, melts at 128—130° and has a faint odour like piperonal as well as the anise-like odour of all triazo- (azoimide) compounds.

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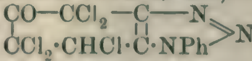
* A name chosen by the authors to designate those groups the presence of which predicates an odorous substance.

Methyl p-*triazobenzoate*, $N_3 \cdot C_6H_4 \cdot CO_2Me$, obtained by the method described in the next abstract, crystallises in large, yellow laminæ, is volatile with steam, melts at 39—40°, and has a characteristic sweet anise-like odour, very similar to that of *methyl* p-*cyanobenzoate*; the latter ester forms colourless leaflets melting at 62°. *Methyl* m-*triazobenzoate* and *methyl* o-*triazobenzoate* are light yellow oils having odours similar to (but weaker than) that of the *p*-compound. p-*Triazoanisole* crystallises in yellowish-white laminæ melting at 36°, and o-*triazoanisole* is a heavy, yellow oil, both having odours similar to those of the triazobenzoates. p-*Triazobenzaldehyde* is a colourless liquid with a strong, pleasant, anise-like odour; p-*triazobenzonitrile*, however, has hardly any odour and crystallises in colourless needles, which melt at 70°. p-*Triazoacetanilide* forms colourless crystals and melts at 124°.

m-*Hydroxyacetophenone*, obtained by the diazotisation of *m*-aminoacetophenone and decomposition of the resulting diazo-compound, crystallises in colourless laminæ, melts at 95°, forms a *methyl* ether, which is a colourless oil boiling at 128—129° under 12 mm. pressure, and unlike the analogous *o*- and *p*-compounds has hardly any odour. m-*Cyanoacetophenone* crystallises in small, white needles, melts at 98—99°, and has no odour; the corresponding m-*acetylbenzoic acid* crystallises in slender, white needles, melts at 172°, is odourless, and forms a *methyl* ester, which is a colourless, odourless oil; m-*triazoacetophenone* is a yellow, odourless oil. R. H. P.

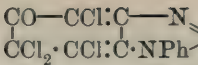
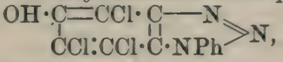
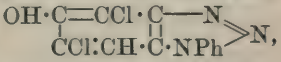
Preparation of Azoimides (Triazo-compounds). By HANS RUPE and KARL VON MAJEWSKI (*Ber.*, 1900, **33**, 3408—3410).—The azoimides corresponding with weak bases are most conveniently prepared by treating a solution of a diazo-salt with potassium hydroxylaminedisulphonate. The method gave good results with *p*-nitroaniline, *m*-nitroaniline, methyl *p*-aminobenzoate, and *p*-bromoaniline. p-*Triazobromobenzene* forms crystals melting at 20° and has a pleasant aromatic odour. Hydroxylamine hydrochloride may be used instead of potassium hydroxylaminedisulphonate, but the results are not quite so good. R. H. P.

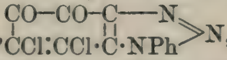
Ketochlorides and Quinones of Phenylaziminobenzene [Phenylbenzotriazole]. By THEODOR ZINCKE and E. PETERMANN (*Annalen*, 1900, **313**, 251—298. Compare Abstr., 1899, i, 135).—*Phenylaziminopentachloroketotetrahydrobenzene*,

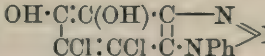


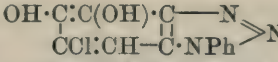
$$\begin{array}{l} CO{-}CCl_2{-}C{-\!\!-}N \\ | \qquad\qquad\quad \| \qquad\quad \rangle N, \\ CCl_2 \cdot CHCl \cdot C \cdot NPh \end{array}$$

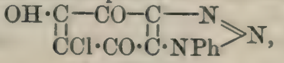
prepared by the action of chlorine on phenylaziminoaminobenzene (Nietzki, Abstr., 1896, i, 164), crystallises in lustrous, colourless needles, and melts at 128—129°; it liberates iodine from potassium iodide, and develops an intense red coloration with aniline.

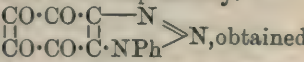
Phenylaziminotetrachloroketodihydrobenzene,  $\left.\begin{array}{l}\text{CO—CCl:C——N}\\ \text{CCl}_2\cdot\text{CCl:C}\cdot\text{NPh}\end{array}\right>\text{N}$, obtained when the foregoing substance is heated alone or with potassium acetate, dissolves readily in organic media, and decomposes when attempts are made to recrystallise it; the compound melts at 173—174°, liberates iodine from potassium iodide, and develops an intense red coloration with aniline. *Phenylaziminotrichlorophenol,*  $\left.\begin{array}{l}\text{OH}\cdot\text{C}{=}\text{CCl}\cdot\text{C——N}\\ \quad\;\;\text{CCl:CCl}\cdot\text{C}\cdot\text{NPh}\end{array}\right>\text{N}$, formed on reducing the last-named substance with stannous chloride, crystallises from glacial acetic acid in pale yellow needles, which melt and decompose at 227°; the *acetyl* derivative forms colourless needles and melts at 128°. *Phenylaziminodichlorophenol,*  $\left.\begin{array}{l}\text{OH}\cdot\text{C}{=}\text{CCl}\cdot\text{C——N}\\ \quad\;\;\text{CCl:CH}\cdot\text{C}\cdot\text{NPh}\end{array}\right>\text{N}$, obtained by reducing the pentachloroketone with stannous chloride, crystallises in colourless, prismatic needles, and melts at 177—178°.

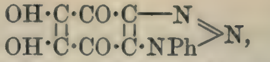
Phenylaziminodichloro-o-quinone,  $\left.\begin{array}{l}\text{CO—CO—C——N}\\ \text{CCl:CCl}\cdot\text{C}\cdot\text{NPh}\end{array}\right>\text{N}$, is formed from trichlorophenol and tetrachloroketone on oxidation with nitric acid, and crystallises in reddish-yellow leaflets having a golden lustre; it melts and decomposes at 210°, and gives a bluish-green solution in sodium hydroxide. The *anilino*-derivative, $C_{18}H_{11}O_2N_4Cl,C_6H_7N$, purified by precipitation with water from solutions in alcohol or acetic acid, melts and decomposes at 130—140°; the *azine*, $C_{18}H_9N_5Cl_2$, prepared from the quinone and *o*-phenylenediamine, crystallises in silky needles, and melts above 250°.

Phenylaziminodichlorocatechol,  $\left.\begin{array}{l}\text{OH}\cdot\text{C:C(OH)}\cdot\text{C——N}\\ \quad\;\;\text{CCl:CCl}\cdot\text{C}\cdot\text{NPh}\end{array}\right>\text{N}$, formed when the quinone is reduced with stannous chloride, crystallises from glacial acetic acid in slender, pale red needles which melt and decompose at 217°; the *diacetyl* derivative forms colourless needles and melts at 187°.

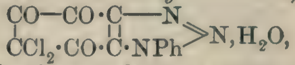
Phenylaziminochlorocatechol,  $\left.\begin{array}{l}\text{OH}\cdot\text{C:C(OH)}\cdot\text{C——N}\\ \quad\;\;\text{CCl:CH—C}\cdot\text{NPh}\end{array}\right>\text{N}$, the other product of reducing the quinone, melts and decomposes at 214—215°.

Phenylaziminochlorohydroxy-p-quinone,  $\left.\begin{array}{l}\text{OH}\cdot\text{C—CO—C——N}\\ \quad\;\;\text{CCl}\cdot\text{CO}\cdot\text{C}\cdot\text{NPh}\end{array}\right>\text{N}$, prepared by the action of sodium carbonate on the dichloro-*o*-quinone, crystallises in lustrous, yellow needles which melt and decompose at 223°; the *acetyl* derivative forms lustrous, yellow needles melting at 135—136°, whilst the *anilino*-derivative, $C_{18}H_3O_3N_4Cl$, and the *eurhodol*, $C_{18}H_{10}ON_5Cl$, decompose at 180° and 200° respectively.

Phenylaziminotetraketotetrahydrobenzene,  $\left.\begin{array}{l}\text{CO}\cdot\text{CO}\cdot\text{C——N}\\ \text{CO}\cdot\text{CO}\cdot\text{C}\cdot\text{NPh}\end{array}\right>\text{N}$, obtained on oxidising the *p*-quinone with nitric acid, crystallises from the concentrated acid in colourless needles which become yellow in light, and melt and decompose at 175°; the *diazine*, $C_{24}H_{13}N_7$, is sparingly soluble in common media, and melts above 260°.

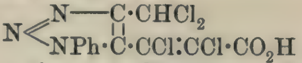
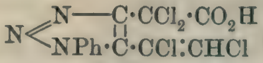
*Phenylaziminodihydroxy-*p*-quinone,*  $\begin{array}{l}\mathrm{OH\cdot C\cdot CO\cdot C—N}\\ \mathrm{OH\cdot C\cdot CO\cdot C\cdot NPh}\end{array}\!\!>\!\mathrm{N}$, formed when the tetraketone is dissolved in sodium carbonate, is a red powder which gradually darkens above 200°, and melts, decomposing, at about 254°.

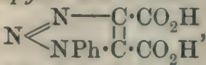
Phenylaziminodichlorotriketotetrahydrobenzene,

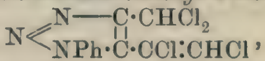


$$\begin{array}{l}\mathrm{CO—CO\cdot C—N}\\ \mathrm{CCl_2\cdot CO\cdot C\cdot NPh}\end{array}\!\!>\!\mathrm{N,H_2O},$$

produced when chlorine is passed into a solution of the chlorohydroxy-*p*-quinone in acetic acid, crystallises in small, white needles and melts, decomposing, at 150—151°; the *azine*, $C_{18}H_{19}ON_5Cl_2$, crystallises from glacial acetic acid in grey, lustrous needles, which sinter above 210°, and decompose at 238°.

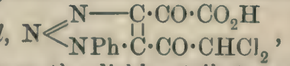
The *acid*,  $\mathrm{N}\!<\!\begin{array}{l}\mathrm{N—C\cdot CHCl_2}\\ \mathrm{NPh\cdot C\cdot CCl{:}CCl\cdot CO_2H}\end{array}$ or  $\mathrm{N}\!<\!\begin{array}{l}\mathrm{N—C\cdot CCl_2\cdot CO_2H}\\ \mathrm{NPh\cdot C\cdot CCl{:}CHCl}\end{array}$, prepared from the pentachloroketone by the action of dilute sodium hydroxide, and of bleaching powder in either acid or alkaline solution, crystallises from alcohol in colourless needles melting at 148°; the *sodium* salt forms transparent prisms, and the *methyl* ester melts at 124°.

1-*Phenyl*-1 : 2 : 3-*triazole*-4 : 5-*dicarboxylic* (n-*phenylpyrro*-1 : 2-*diazole-dicarboxylic, phenylaziminoethylenedicarboxylic*) *acid*,  $\mathrm{N}\!<\!\begin{array}{l}\mathrm{N—C\cdot CO_2H}\\ \mathrm{NPh\cdot C\cdot CO_2H}\end{array}$, resulting from the oxidation of the foregoing acid with potassium permanganate, has been already described by Michael (Abstr., 1893, i, 570). 1-*Phenyl*-4-*dichloromethyl*-5-*dichloroethylene*-1 : 2 : 3-*triazole* (n-*phenylimino*-1 : 2-*diazole*-3-*dichloromethyl*-4-*dichloroethylene*),



$$\mathrm{N}\!<\!\begin{array}{l}\mathrm{N—C\cdot CHCl_2}\\ \mathrm{NPh\cdot C\cdot CCl{:}CHCl}\end{array},$$

produced when the monocarboxylic acid is heated alone or with acetic anhydride, crystallises from glacial acetic acid and melts at 95—96°.

The *aδ-diketocarboxylic acid*,  $\mathrm{N}\!<\!\begin{array}{l}\mathrm{N—C\cdot CO\cdot CO_2H}\\ \mathrm{NPh\cdot C\cdot CO\cdot CHCl_2}\end{array}$, prepared by the action of sodium carbonate on the dichlorotriketone, crystallises in lustrous, colourless needles which darken above 105°, and melt and decompose at 130°; phenylhydrazine converts it into the *diphenylhydrazone*, $C_{24}H_{18}O_2N_7Cl$, which forms reddish-brown, crystalline granules sintering above 110°. M. O. F.

4-Methyldeoxyxanthine and Deoxyheteroxanthine. By JULIUS TAFEL and ARTHUR WEINSCHENK (*Ber.*, 1900, 33, 3369—3377. Compare Abstr., 1900, i, 121; ii, 588).—When 4-methylxanthine is dissolved in 50 per cent. sulphuric acid and reduced electrolytically at 1—14° between prepared lead electrodes with a current concentration of 120 amperes, the *sulphate* of 5-*oxy*-4-*methyl*-6 : 7-*dihydropurine* (4-*methyldeoxyxanthine*) separates; this salt and the *picrate* were analysed. The base itself crystallises with $1H_2O$, and decomposes at 210—220° without melting; although neutral in reaction to litmus, it dissolves in dilute alkalis. It is oxidised by bromine in acetic acid solution (lead peroxide is not suitable) to *5-oxy-4-methylpurine*; this base and its *sulphate* and *picrate* were prepared, and the last two were analysed.

Heteroxanthine was also reduced in the manner just described; in this case no sulphate separates. The product, 5-*oxy*-1-*methyl*-6:7-*dihydropurine* (deoxyheteroxanthine), decomposes at 260—264° without melting; it is feebly alkaline to litmus, and does not dissolve in dilute alkalis; the *hydrochloride*, *sulphate*, and *picrate* were prepared and analysed. The base is oxidised either by lead peroxide or by bromine, in acetic acid solution, to 5-oxy-1-methylpurine (E. Fischer, Abstr., 1899, i, 175). C. F. B.

Isomeric Change of Azoxybenzene. By EUGEN BAMBERGER (*Ber.*, 1900, **33**, 3192—3193).—When azoxybenzene is converted into *p*-hydroxyazobenzene by warm sulphuric acid (Wallach and Belli, Abstr., 1880, 556), a very small quantity of *o*-hydroxyazobenzene is formed and may be isolated by the process already described (see following abstract). A. L.

Action of Diazobenzene on Phenol and Synthesis of *o*-Hydroxyazobenzene. By EUGEN BAMBERGER (*Ber.*, 1900, **33**, 3188—3192).—*o*-Hydroxyazobenzene is obtained in small quantity by the action of diazobenzene on phenol and may be separated from the para-derivative by distillation with steam and purified by means of its copper salt, which is very sparingly soluble in alcohol. It is identical with the substance obtained from nitrosobenzene (Abstr., 1900, i, 531).

o-*Methoxyazobenzene*, $OMe\cdot C_6H_4\cdot N_2\cdot Ph$, is obtained on adding *o*-anisidine to nitrosobenzene dissolved in acetic acid. It crystallises in groups of orange-red, compact needles melting at 40—41°, dissolves readily in most organic media even in the cold, and is converted into *o*-hydroxyazobenzene by aluminium chloride.

o-*Hydroxybenzeneazo*-p-*toluene*, $OH\cdot C_6H_4\cdot N_2\cdot C_6H_4Me$, produced in small quantity when *p*-diazotoluene reacts with phenol, crystallises from boiling water in thin, shining, irregular yellow tablets or leaflets with a bronze lustre melting at 100—105°. It dissolves readily in organic solvents and sparingly in water. Its solution in alkali is orange-red. The *copper* salt, which is sparingly soluble in boiling alcohol, forms brown, silky needles which have a green, metallic lustre. On reduction with zinc dust and aqueous ammonium chloride, the dye is converted into *o*-aminophenol and *p*-toluidine. A. L.

Composition of Proteids. By ALBRECHT KOSSEL and W. KUTSCHER (*Zeit. physiol. Chem.*, 1900, **31**, 165—214).—An important contribution to proteid chemistry, but which hardly admits of abstraction. Important quantitative results concerning the way in which different fractions of the nitrogen are combined, and the yield of such decomposition products as amino-acids, ammonia, hexon bases, &c., are given, together with quantitative methods. Protamines, proteids proper, and albuminoids are all brought under review. W. D. H.

Decomposition Products of Proteids. By FR. KUTSCHER (*Zeit. physiol. Chem.*, 1900, **31**, 214—226).—Hausmann's method (Abstr., 1899, i, 653; 1900, i, 317) of determining the way in which the nitrogen is combined in proteids is untrustworthy. W. D. H.

NOTE BY ABSTRACTOR.—This has been pointed out previously by Y. Henderson (Abstr., 1900, i, 265).

The Carbohydrate Group of Crystallised Egg-Albumin. By LEO LANGSTEIN (*Zeit. physiol. Chem.*, 1900, 31, 49—57).—It is shown that the reducing substance which can be obtained from crystallised egg-albumin is glucosamine. The direct action of concentrated mineral acid on egg-albumin does not split off the reducing substance, because of the simultaneous production of ammonia. After treatment with alkali, as Pavy first showed, the reducing substance is obtainable. W. D. H.

The Phosphorus of Nucleins. By ALBERTO ASCOLI (*Zeit. physiol. Chem.*, 1900, 31, 156—160).—Neither in leuco-nuclein nor in casein is any of the phosphorus contained in the form of metaphosphoric acid. W. D. H.

A New Decomposition Product of Yeast Nuclein. By ALBERTO ASCOLI (*Zeit. physiol. Chem.*, 1900, 31, 161—164).—Thymin has been obtained from the nucleic acid from thymus, spleen, salmon sperm, and herring roe. The amount of materal hitherto obtained from yeast nuclein did not admit of analysis. In the present research, thymin was obtained by W. Jones' method (Abstr., 1900, i, 572) from thymus, and a similar material from yeast nuclein; the latter substance was not thymin, but uracil. W. D. H.

Constitution of Thymin. By H. STEUDEL (*Zeit. physiol. Chem.*, 1900, 30, 539—541. Compare Abstr., 1900, i, 467). When thymin is methylated by Hoffmann's method (Abstr., 1890, 31) a *product*, $C_5H_4Me_2O_2N_2$, is obtained which is isomeric with Behrend's trimethyluracil (Abstr., 1886, 339). It crystallises from alcohol in needles melting at 153°.

When thymin is nitrated and then reduced, a substance is obtained which gives Weidel's reaction with chlorine water and ammonia; the author concludes that the presence of a pyrimidine ring in thymin is thus established. J. J. S.

Antipeptone. By FR. KUTSCHER (*Ber.*, 1900, 33, 3457—3460).—A polemical paper in reply to Siegfried (this vol., i, 57).

J. J. S.

Expressed Yeast-cell-plasma (Buchner's Zymase). By EDUARD BUCHNER (*Ber.*, 1900, 33, 3311—3315).—The author criticises several of the numerical results obtained by Macfadyen, Morris, and Rowland (this vol., i, 59), and points out that the considerable amount of autofermentation observed by them was probably due to the presence of glycogen in the juice. The juice obtained by the author underwent very little autofermentation, the amount of carbon dioxide thus evolved being always less than one-tenth of that evolved in the presence of sugar. A. H.

Organic Chemistry.

Composition of Shale Naphtha. By Basil Steuart (*J. Soc. Chem. Ind.*, 1900, **19**, 986—989).—The olefines were removed by successive treatment with concentrated sulphuric acid and aqueous sodium hydroxide, and the aromatic hydrocarbons by shaking with a mixture of sulphuric and nitric acids; the nature and amount of the olefines were not determined, but they appear to be present in larger quantity than in natural petroleum. After the foregoing treatment, the naphtha boiling between 20° and 105° was repeatedly fractionated. *n*-Hexane was by far the principal hydrocarbon present, traces only of *iso*hexane being found, along with, possibly, methylpentamethylene; the *n*-hexane was purified by heating for three days with fuming nitric acid, when the latter was found to contain propionic and succinic acids with a trace of oxalic acid. *n*-Heptane and *iso*heptane were present to a considerable extent but could not be separated from one another by fractional distillation; the high values for the sp. gr. of the heptane fractions between 89° and 100° appear to indicate the presence of, possibly, both hexamethylene and methylhexamethylene and the absence of dimethylpentamethylene. The difficulty experienced in separating the *n*-heptane and *iso*heptane may be due to the presence of the isomeric γ-ethylpentane (triethylmethane) boiling at 96°, but this hydrocarbon has not yet been identified in American or Russian petroleum.

n-Pentane was present in small proportion compared with the hexanes and heptanes, and *iso*pentane in small proportion to *n*-pentane. The sp. gr. and vapour density of a small fraction boiling between 48° and 57° appear to indicate the presence in small quantities of pentamethylene; a small fraction boiling between 38° and 42° similarly appeared to contain methyltetramethylene.

The greatest proportion of benzene was found in the original fractions boiling between 70° and 75° and 65° and 70°, and was separated as *m*-dinitrobenzene; the fraction 75—80° contained only traces of benzene, owing to the bulk of the latter having distilled at a lower temperature along with the hexane (compare Young and Jackson, Trans., 1898, **73**, 922). Benzene appears to constitute 2·6 per cent. of the original fractions boiling between 55° and 75°; it is probable, however, that an additional quantity may have been removed by the preliminary treatment to eliminate olefines. Toluene forms about the same proportion of the fraction from 95—105°, its distilling below its boiling point being due to the presence of heptane (compare *loc. cit.*). W. A. D.

Electrolytic Synthesis of Organic Substances. By Karl Elbs and Fritz Foerster (*Zeit. Elektrochem.*, 1900, 7, 341).—A reply to Dony-Hénault (Abstr., 1900, i, 577) with reference to the electrolytic formation of iodoform. T. E.

Derivatives of Tetradecylacetylene. By FRIEDRICH KRAFFT and G. HEIZMANN (*Ber.*, 1900, 33, 3586—3590. Compare Abstr., 1892, 1163).—*Tetradecylacetylene tetrabromide*, $C_{14}H_{29}\cdot CBr_2\cdot CHBr_2$, a colourless liquid which cannot be distilled under 15 mm. pressure, is prepared by mixing together tetradecylacetylene and bromine at a low temperature and then gradually heating the mixture to 60°. The *copper* compound, $C_{14}H_{29}\cdot C{\vdots}C\cdot Cu\cdot OH$, is a greenish-grey substance produced by shaking together the hydrocarbon and ammoniacal cuprous chloride solution; the *mercurichloride*, $C_{14}H_{29}\cdot C{\vdots}C\cdot HgCl$, is a white compound, whilst the *mercuronitrate*, $C_{14}H_{29}\cdot C{\vdots}C\cdot Hg_2\cdot NO_3$, is white, turning grey on exposure to light. The *sodium* derivative, $C_{14}H_{29}\cdot C{\vdots}CNa$, is a yellowish-white substance regenerating the hydrocarbon on treatment with water or methyl alcohol.

Nitrotetradecylacetylene, $C_{16}H_{29}\cdot NO_2$, produced by slowly adding fuming nitric acid to tetradecylacetylene cooled to $-16°$, yields *aminotetradecylacetylene*, $C_{14}H_{29}\cdot C{\vdots}C\cdot NH_2$, on reduction with zinc dust and acetic acid; this base is a white, crystalline mass melting at 41—42°, and boiling at 195° under 15 mm. pressure; its *platinichloride* forms a yellow, flocculent precipitate.

Tetradecylacetylenesulphonic acid, $C_{14}H_{29}\cdot C{\vdots}C\cdot SO_3H$, is obtained in the form of its barium salt, $(C_{16}H_{29}SO_3)_2Ba$, by mixing the hydrocarbon with concentrated sulphuric acid, neutralising the solution with dilute sodium hydroxide solution, precipitating the sulphonate by means of sodium chloride, redissolving this product in hot water, and reprecipitating with barium chloride.

Tetradecylacetylenecarboxylic acid (*tetradecylpropiolic acid*), $C_{14}H_{29}\cdot C{\vdots}C\cdot CO_2H$, prepared by passing carbon dioxide over sodium tetradecylacetylide heated at 120°, crystallises from dilute methyl alcohol in white leaflets melting at 44—45°; when distilled under 15 mm. pressure, it decomposes into carbon dioxide and tetradecylacetylene. Silver nitrate in aqueous ammoniacal solution forms the *silver* salt, $C_{14}H_{29}\cdot C{\vdots}C\cdot CO_2Ag$.

Tetradecylpropiolamide, $C_{14}H_{29}\cdot C{\vdots}C\cdot CO\cdot NH_2$, produced by adding a mixture containing equivalent proportions of phosphorus pentachloride and the acid to cold concentrated ammonia, crystallises from absolute alcohol in leaflets melting at 76—77°; the *benzoyl* derivative melts at 114—115°.

Tetradecylbenzoylacetylene, $C_{14}H_{29}C{\vdots}C\cdot COPh$, a very unstable ketone, it obtained by condensing crude tetradecylpropiolic chloride with benzene in the presence of aluminium chloride; it distils at 145° in a high vacuum, and solidifies to a yellowish-white, waxy mass. G. T. M.

Presence of Methyl Alcohol in the Fermented Juice of several Fruits. By JULES WOLFF (*Compt. rend.*, 1900, 131, 1323—1324. Compare Abstr., 1899, ii, 387).—The fermented juice of black currants, plums, mirabelles, cherries, apples, or grapes contains methyl alcohol, but the unfermented juice does not, except black currant juice, which contains it in small quantities. Rum and whisky do not contain methyl alcohol, but traces of it are present in brandy.

H. R. LE S.

Absence of Methyl Alcohol in Rum. By Henri Quantin (*J. Pharm.*, 1900, [vi], **12**, 505—507. Compare Abstr., 1899, ii, 387, and preceding abstract).—Formaldehyde, methyl formate, and methyl alcohol were found to be absent from the distillates obtained by the fractional distillation of 85 hectolitres of rum. H. R. Le S.

Hydrolysis of Ethyl Nitrate by Water. By Eugen von Biron (*J. Russ. Phys. Chem. Soc.*, 1900, **32**, 656—667).—The solubility of ethyl nitrate in 100 parts of water between 55° and 85° is given by the following formula, in which t represents the temperature: $2{\cdot}2239 - 0{\cdot}03642\,t + 0{\cdot}0003512\,t^2$.

The hydrolysis of ethyl nitrate was studied in an aqueous solution kept saturated at 70°. The reaction is unimolecular, so that if x be the quantity of nitric acid formed after a time, θ (hours), and K the velocity constant of the reaction, $dx/d\theta = K$, whence $K = (x - x_0)/\theta$. The results show that the value of K increases from about 0·134 when $\theta = 5$ to 0·150 when $\theta = 114$, indicating that the nitric acid formed exerts an accelerating influence on the hydrolysis. Taking k_1 as the constant of the hydrolysis of ethyl nitrate by water and k_2 as that of the accelerating action of the nitric acid, C representing the constant concentration, the velocity of the reaction is represented by: $dx/d\theta = (k_1 + k_2)C$. The values of k_1 and k_2 calculated on the basis of the above measurements are: $k_1 = 0{\cdot}004246$, which means that in a solution of constant concentration water hydrolyses in 1 hour 0·004246 of the total quantity of ethyl nitrate present; $k_2 = 0{\cdot}0135$ (for normal acid), the total action of the acid and water being given by the constant $(k_1 + k_2) = 0{\cdot}0177$. Other experiments with non-saturated solutions of ethyl nitrate, with and without the addition of nitric acid, confirm these numbers. These results are quite different from those obtained in the hydrolysis of esters of organic acids; thus Ostwald (Abstr., 1884, 581), in determining the velocity of hydrolysis of methyl acetate by normal nitric, hydrochloric, and other acids, did not take into account the action of the water present. From numbers given by Ostwald, it is seen that at 25° water hydrolyses in 30 days some 20—25 per cent. of the methyl acetate in solution, whilst with the same initial concentration of the ester, normal acetic acid hydrolyses 67 per cent. in the same time. The ratio between these two velocities is of the same order as in the hydrolysis of ethyl nitrate by nitric acid, although the actual velocities are widely different in the two cases. T. H. P.

Action of Ethyl Iodide on Silver Nitrate. By Eugen von Biron (*J. Russ. Phys. Chem. Soc.*, 1900, **30**, 667—673).—When ethyl iodide is gradually added to powdered silver nitrate, the mixture being kept cool, nearly the theoretical yield of ethyl nitrate is obtained. In presence of water, however, part of the ethyl nitrate formed is converted into alcohol and nitric acid (see preceding abstract), whilst if the reaction is carried out in absolute alcoholic solution, ether and nitric acid are formed along with the ethyl nitrate, as has been already shown by Nef (Abstr., 1900, i, 4). The results of Bertrand (*Bull. Soc. Chim.*, 1880, **33**, 556), who, on boiling ethyl iodide in absolute alcohol with silver nitrate, obtained ethyl nitrate and nitrite and acetaldehyde, are explained by the fact that he distilled off the excess of alcohol and ethyl nitrate from the resultant products, the nitric acid thus being concentrated and acting on the remaining alcohol according to the equation: $2EtOH + HNO_3 = MeCHO + EtNO_2 + 2H_2O$. Nef (*loc. cit.*) explains the action of silver nitrate on ethyl iodide in alcoholic solution as due to the preliminary formation of methylene derivatives, caused by the splitting off of hydrogen and iodine atoms from the same carbon atom of the ethyl iodide, this and the subsequent reactions being expressed by the following equations: (1) $Me{\cdot}CH_2I \rightleftarrows Me{\cdot}CH + HI$, (2) $HI + AgNO_3 = AgI + HNO_3$, (3) $Me{\cdot}CH + HNO_3 = Me{\cdot}CH_2{\cdot}NO_3$, (4) $Me{\cdot}CH + Me{\cdot}CH_2{\cdot}OH = Et_2O$. According to this view, the whole reaction should be unimolecular, since reaction (2), being ionic, has an immense velocity, and removes all the hydrogen iodide formed by reaction (1), which would hence proceed to an end. It has, however, been shown by Chiminello (Abstr., 1896, ii, 354) that the action of ethyl iodide on silver nitrate is bimolecular at 0°, although at higher temperatures, where the reaction proceeded much more rapidly, the velocity constant calculated for a bimolecular reaction was found to increase appreciably; this increase is shown by the author to be due to the rapid development of heat by the reaction, and the consequent heating of the solutions, since by using solutions with less concentration, in which the velocity of reaction is correspondingly diminished, he finds the reaction to be strictly bimolecular. From these considerations and also from the facts (1), that in the reaction in which *tert*-butyl iodide takes part (also considered by Nef) no dissociation with formation of a methylene derivative is possible, and (2), that with propyl iodide and silver nitrate in alcoholic solution, ethyl propyl ether is obtained, whilst with *iso*propyl iodide, ethyl *iso*propyl ether is formed, whereas Nef's scheme would lead to the formation of ethyl *iso*propyl ether in both cases, the author concludes that Nef's views are erroneous and that the action of ethyl iodide on silver nitrate is one of double decomposition. The formation of ether in this reaction is assumed to be due to the action of alcohol on the ethyl nitrate *in statu nascendi*.

T. H. P.

α-Chlorovaleric Acids. By Léon Servais (*Bull. Acad. Roy. Belg.*, 1900, 695—724).—α-Hydroxyvaleronitrile, formed by the interaction of butaldehyde with hydrogen cyanide, readily reacts with phosphorus pentachloride to form *α-chlorovaleronitrile*, $CH_2Me{\cdot}CH_2{\cdot}CHCl{\cdot}CN$, a slightly yellow liquid boiling at 161°. *α-Chlorovaleric acid*, obtained on hydrolysis with concentrated hydrochloric acid, melts at −15°, boils at 132—135° under 32 mm. and at 222° under 763 mm. pressure, has a sp. gr. 1·141 at 13·2°, n_D 1·44807 at 11°, and is insoluble in water. The *chloride*, $CH_2Me{\cdot}CH_2{\cdot}CHCl{\cdot}COCl$, is a pungent, fuming liquid; it boils at 155—157° under 763 mm. pressure, and has a sp. gr. 1·246. *Ethyl α-chlorovalerate* is a colourless oil with an agreeable mint-like odour; it boils at 185° under 752 mm. pressure, has a sp. gr. 1·040 at 11·8°, and n_D 1·43071 at 11°.

α-Chloroisovaleronitrile, $CHMe_2{\cdot}CHCl{\cdot}CN$, obtained from α-hydroxy*iso*valeronitrile and phosphorus pentachloride, boils at 154—155° under 750 mm. pressure; the corresponding *bromo*-derivative distils and decomposes at 175—180° under a pressure of 754 mm. *α-Chloro-*

iso*valeric acid* is a crystalline mass which melts at 16° and boils at 125—126° under 32 mm., and at 210—212° with slight decomposition under 756 mm. pressure; it has a sp. gr. 1·135 at 13·2° and n_D 1·44496 at 11°. The *chloride*, $CHMe_2·CHCl·COCl$, is a pungent liquid of sp. gr. 1·135 at 13·2°, and boils at 148—149° under 759 mm. pressure. *Ethyl* α*-chloro*iso*valerate* has a penetrating, mint-like odour, boils at 177—179° under 756 mm. pressure, has a sp. gr. 1·021 at 13·2° and n_D 1·42951 at 11°.

α*-Chloro-α-methylbutyronitrile*, CMeEtCl·CN, prepared by the action of phosphorus pentachloride on the cyanohydrin derived from methyl ethyl ketone, is a colourless, mobile liquid which boils unchanged at 55—60° under 32 mm. and at 120—135° with decomposition under 762 mm. pressure; it has a sp. gr. 0·8969 at 15°. α*-Chloro-α-methylbutyric acid* boils at 123—124° under 36 mm. pressure, has a sp. gr. 1·101 at 10° and n_D 1·45077 at 11°; it distils at 200—205° under 754 mm. pressure, with loss of hydrogen chloride, and crystals of a methylcrotonic acid (?) separate from the distillate. The *chloride*, CMeEtCl·COCl, is a fuming liquid, boiling at 143—144° under 749 mm. pressure, and having a sp. gr. 1·187 at 14°. *Ethyl α-chloro-α-methylbutyrate* boils at 175° under 747 mm. pressure, has a sp. gr. 1·069 at 14°, and n_D 1·43683 at 11°.

The relationship between the boiling points of these compounds is discussed at some length. W. A. D.

Preparation of the Higher Acid Anhydrides $(C_nH_{2n-1}O)_2O$. By Friedrich Krafft and W. Rosiny (*Ber.*, 1900, **33**, 3576—3579).—The anhydrides of the higher fatty acids are readily obtained by the action of the acid chlorides on the alkali salts when these compounds are thoroughly dried and purified.

n-*Heptoic anhydride*, $(C_7H_{13}O)_2O$, is a colourless, oily liquid boiling at 164·5° under 15 mm. pressure; it solidifies on cooling, and melts at 17°; it has a characteristic odour resembling that of ozone, and absorbs moisture from the atmosphere, becoming converted into *n*-heptoic acid.

n-*Octoic anhydride*, $(C_8H_{15}O)_2O$, boils at 186° under 15 mm. pressure, and melts at -1°.

n-*Nonoic anhydride*, $(C_9H_{17}O)_2O$, forms a white, crystalline mass melting at 16° and boiling at 207° under 15 mm. pressure.

n-*Lauric anhydride* (n-*dodecoic anhydride*), $(C_{12}H_{23}O)_2O$, obtained in hard, white crystals melting at 41°, boils at 166° when distilled by the aid of von Babo's mercury-air pump.

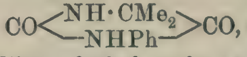
Myristic anhydride (*tetradecoic anhydride*), $(C_{14}H_{27}O)_2O$, forms white crystals, melts at 51°, and boils at 198° in a high vacuum.

Palmitic anhydride (*hexadecoic anhydride*) is a white solid, the melting point of which lies close to that of palmitic acid.

Phenylheptadecenoic acid, $C_6H_5·C_{16}H_{30}·CO_2H$, prepared by heating a mixture of benzaldehyde, palmitic anhydride, and dry sodium palmitate up to 170°, crystallises in slender needles and melts at 87—88°; the replacement of palmitic anhydride by acetic anhydride lessens the yield and purity of the product. The *silver* salt, $C_{23}H_{25}O_2Ag$, obtained by adding silver nitrate to the ammoniacal solution of the acid, forms a voluminous precipitate which becomes crystalline on repeated washing. G. T. M.

Action of Reducing Agents on the Two Isomeric Ethyl Nitrodimethylacrylates. By LOUIS BOUVEAULT and A. WAHL (*Compt. rend.*, 1900, **131**, 1211—1213. Compare this vol., i, 4).—The α-isomeride, $CMe_2{:}C(NO_2){\cdot}CO_2Et$, yields ethyl dimethylacrylate when treated with stannous chloride or tin and hydrochloric acid, and gives rise to products very soluble in water by the action of sodium sulphite or bisulphite. Sodium nitrodimethylacrylate is produced from the ester by the action of sodium and moist ether, and the acid set free by the action of hydrochloric acid loses carbon dioxide and gives rise to a nitro*iso*butylene, probably identical with the product of direct nitration (Haitinger, Abstr., 1879, 700).

Ethyl aminodimethylacrylate, $CMe_2{:}C(NH_2){\cdot}CO_2Et$, produced by the action of aluminium amalgam on a moist ethereal solution of the α-nitro-ester, is a colourless liquid with an unpleasant odour; it boils at 93—95°, and has a sp. gr. 1·018 at 0°/4°. The compound is basic, and dissolves in dilute acids; it is slightly soluble in water and is miscible with the ordinary organic solvents. Its *carbamide* and *phenylcarbamide* crystallise in needles melting respectively at 175—176° and 130°.

iso*Propenylphenylhydantoin*,  $CO<\substack{NH\cdot CMe_2\\ NHPh}>CO$, obtained by boiling the phenylcarbamide with dilute alcohol, melts at 225—226°.

Phenylcarbaminodimethylacrylic acid, produced by the action of sodium hydroxide solution on the phenylcarbamide, melts at 195—196°; the reaction also gives rise to a certain amount of the preceding compound. G. T. M.

Condensation of Ketones with Ethyl Cyanoacetate. By GUSTAV KOMPPA (*Ber.*, 1900, **33**, 3530—3534).—An ice-cold mixture of pure, dry acetone (1 mol.), and ethyl cyanoacetate (2 mols.), when treated with a few drops of diethylamine, undergoes condensation which is complete after the mixture has been left at the ordinary temperature for a month, and then gradually heated on the water-bath for several hours; when distilled under 10 mm. pressure, it yields a fraction boiling at 100—120°, consisting mainly of ethyl dimethylmethylenecyanoacetate, and a fraction 120—175° containing mainly ethyl dimethylmethylenedicyanoacetate.

Ethyl dimethylmethylenecyanoacetate [*ethyl α-cyano-β-methylcrotonate*], $CMe_2{:}C(CN){\cdot}CO_2Et$, is a colourless, mobile oil distilling at 108° under 10 mm. pressure, and solidifying to a crystalline mass melting at 28°, and readily soluble in all organic solvents. It is readily oxidised, but does not combine with bromine.

Ethyl dimethylmethylenedicyanoacetate, [*ethyl αα′-dicyano-ββ-dimethylglutarate*], $CMe_2[CH(CN){\cdot}CO_2Et]_2$, is a thick oil distilling at 186—188° under 10 mm. pressure; it crystallises from ether and light petroleum in four-sided plates melting at 53—54°. With sodium ethoxide, it yields a yellow, crystalline *sodium* derivative; when hydrolysed with 50 per cent. sulphuric acid, it yields ββ-dimethyl glutaric acid. J. J. S.

Transformation of *ικ*-Undecenoic Acid into *θι*-Undecenoic Acid and Brassylic Acid. By FRIEDRICH KRAFFT and R. SELDIS (*Ber.*, 1900, **33**, 3571—3575).—*ι-Bromo-θι-undecenoic acid,*

$$CMeBr{:}CH\cdot[CH_2]_7\cdot CO_2H,$$

prepared by saturating a carbon disulphide solution of undecolic acid (m. p. 59·5°) at 50° with hydrogen bromide, is an oil solidifying at low temperatures and boiling with slight decomposition at 202° under 16 mm. pressure. *θι-Undecenoic acid,* $CHMe{:}CH\cdot[CH_2]_7\cdot CO_2H$, obtained by reducing the preceding compound in alcoholic solution with sodium containing a trace of mercury, aluminium, or iron, boils at 165° under 10 mm. pressure, and melts below 19°. The new acid is distinguished from its isomeride, *ικ*-undecenoic acid, by its lower melting point and by its behaviour towards an acetic acid solution of chromium trioxide, the former compound yielding azelaic acid, whilst the latter gives rise to sebacic acid. The *θι*-acid forms a *dibromide*, $C_{11}H_{20}Br_2O_2$, an *amide*, $C_{11}H_{19}ONH_2$, melting at 86—87°, an insoluble *silver* salt, and a *barium* salt closely resembling that of the *ικ*-isomeride.

Komppa (Abstr., 1900, i, 201) successively prepared from methyl bromo-undecoate by the malonic ester synthesis a methyl diethyl undecanetricarboxylate boiling at 223—224° under 10 mm. pressure, an oily undecanetricarboxylic acid, and a normal undecamethylenedicarboxylic acid melting at 82°; as this dicarboxylic acid appeared to be isomeric and not identical with brassylic acid, he concluded that the latter must contain a branched chain. The authors find, on repeating this work, that the tricarboxylic ester boils at 233—234° under 10 mm. pressure, and that the acid is a solid which, on heating, yields brassylic acid melting at 113—114°, and corresponding in every respect with the product obtained from erucic acid. G. T. M.

Derivatives of the Higher Unsaturated Carboxy-acids. By FRIEDRICH KRAFFT and F. TRITSCHLER (*Ber.*, 1900, **33**, 3580—3585). —*ικ-Undecenoic chloride*, $C_{10}H_{19}\cdot COCl$, obtained in quantitative yield by the action of phosphorus pentachloride on *ικ*-undecenoic acid, is an oil boiling at 128·5° under 14 mm. pressure; the *anhydride*, $(C_{11}H_{19}O)_2O$, produced by heating together a mixture of the preceding compound and dry sodium undecenoate, melts at 13—13·5°, and boils at 170—179° in a high vacuum; its *tetrabromide*, $(C_{10}H_{19}Br_2\cdot CO)_2O$, melts at 36·5°. *ικ-Undecenamide*, $C_{11}H_{19}O\cdot NH_2$, prepared by treating the chloride with ice-cold aqueous ammonia, crystallises in white scales and melts at 87°. *ικ-Undecenonitrile*, $C_{10}H_9\cdot CN$, produced when the amide is warmed with phosphorus pentachloride, boils at 129—130° under 14 mm. and at 257° under the ordinary pressure.

Amino-ικ-undecylene, $C_{11}H_{21}\cdot NH_2$, a colourless liquid solidifying in a freezing mixture and boiling at 123° under 16 mm. pressure and at 238—240° under the ordinary pressure, is formed by reducing *ικ*-undecenonitrile with sodium and absolute alcohol; its *benzoyl* derivative crystallises from benzene in leaflets, and melts at 41—42°; its *phenylthiocarbamide* forms colourless leaflets melting at 48°.

Diundecenylthiocarbamide, produced from the base and carbon disulphide, crystallises in white leaflets and melts at 50·5°. *Undecenamidoxime*, $C_{10}H_{19}\cdot C(NH_2){:}NOH$, formed by the addition of hydroxylamine to the nitrile, crystallises from benzene in lustrous, white leaflets melting at 69°.

Elaidic chloride, $C_{17}H_{33}\cdot COCl$, is a colourless, slightly fuming liquid boiling with partial decomposition at 216° under 13 mm. pressure; it solidifies in a freezing mixture; its *amide* melts at 89—90°; *elaidonitrile* melts at – 1°, and boils at 213—214° under 16 mm. pressure.

Elaidamine, $C_{18}H_{35}\cdot NH_2$, forms a white, crystalline mass melting at 25° and boiling at 194—195° under 13 mm. and at 338—340° under the ordinary pressure; it rapidly absorbs carbon dioxide from the air. The *hydrochloride* crystallises in lustrous, white scales, and decomposes at 185°; the *platinichloride* and the *benzoyl* derivative form yellow scales and lustrous leaflets respectively, the latter melting at 63—64°. *Dielaidylthiocarbamide*, $CS(NH\cdot C_{18}H_{35})_2$, and *phenylelaidylthiocarbamide*, $C_{18}H_{35}NH\cdot CS\cdot NHPh$, crystallise in white leaflets melting respectively at 73° and 65°.

Oleic chloride is a colourless liquid boiling at 213° under 13·5 mm. pressure; the *amide* melts at 75°, and yields elaidonitrile on treatment with phosphorus pentachloride.

Brassic chloride, $C_{21}H_{41}\cdot COCl$, yields the *amide* melting at 94°. *Brassonitrile*, $C_{21}H_{41}\cdot CN$, melts at 21—22° to a colourless, inodorous liquid boiling at 257° under 17 mm. pressure. *Brassamine*, $C_{22}H_{43}\cdot NH_2$, melts at 45—46°, and boils at 250° under 11 mm. pressure; its *benzoyl* derivative crystallises in lustrous leaflets and melts at 74—75°; the *hydrochloride* and *platinichloride* are described, the former melting and decomposing at 130°. *Erucamide*, melting at 78—79°, when treated with phosphorus pentachloride, yields brassonitrile.
G. T. M.

Lactic Acid in Beet-molasses. By A. Schöne and Bernhard Tollens (*Zeit. Ver. deut. Zuckerind.*, 1900, 980—981).—Lactic acid is invariably found in beet-molasses, and owes its origin to the boiling of the sucrose solution with lime in the process of defecation. T. H. P.

Action of Amyl Formate on Ethyl Sodiocyanoacetate. By E. Grégoire de Bollemont (*Bull. Soc. Chim.*, 1901, [iii], 25, 15—18).—The principal product of the action of amyl formate on ethyl sodiocyanoacetate at 100° is not ethyl formylcyanoacetate, which might be expected to be formed, but a *compound*, $CN\cdot C(:CH\cdot ONa)\cdot CO_2\cdot C_5H_{11}$, in the production of which an interchange of the amyl and ethyl groups has taken place, whilst the formyl group must be considered, from analogy with homologous compounds (see following abstracts), to have assumed the enolic form. The *barium* salt, $(C_9H_{12}O_3N)_2Ba$, in which form the compound was isolated, crystallises in nacreous leaflets, and the *silver* salt in tufts of slender needles. The former is identical with the barium salt obtained from the product of the action of amyl formate on amyl sodiocyanoacetate.
N. L.

Ethoxy- and Methoxy-methylenecyanoacetic Esters. By E. Grégoire de Bollemont (*Bull. Soc. Chim.*, 1901, [iii], 25, 18—28).—The following compounds were prepared by heating together molecular proportions of ethyl (or methyl) orthoformate with various alkyl cyanoacetates in the presence of acetic anhydride.

Ethyl ethoxymethylenecyanoacetate [*a-cyano-β-ethoxyacrylate*]

$OEt{\cdot}CH{:}C(CN){\cdot}CO_2Et$, from ethyl cyanoacetate and ethyl orthoformate, crystallises from boiling alcohol in large, colourless needles melting at 52—53° and boiling at 190—191° under 30 mm. pressure. The *methyl* ester crystallises from alcohol in large, transparent tablets melting at 28° and boiling at about 200° under 32 mm. pressure; it has a sp. gr. 1·1255 at 23°/4°. Determinations of the molecular refraction and dispersion of this compound, both in the pure state and when dissolved in toluene, gave values considerably higher than those calculated from Brühl's data, a result which is probably to be explained by the presence of the ethylenic linking. The *propyl* ester forms large, colourless crystals melting at 31° and boiling at 189° under 15 mm. pressure. The *amyl* ester could only be obtained as an oily liquid boiling at about 211° under 35 mm. pressure.

Methyl methoxymethylenecyanoacetate [*α-cyano-β-methoxyacrylate*], $OMe{\cdot}CH{:}C(CN){\cdot}CO_2Me$, obtained by the action of methyl orthoformate on methyl cyanoacetate and also by the action of methyl iodide on the silver derivative, $OAg{\cdot}CH{:}C(CN){\cdot}CO_2Me$, derived from methyl cyanoethoxyacrylate, crystallises in slender needles melting at 88° and boiling at 185° under 25 mm. pressure. The *ethyl* ester crystallises in small prisms melting at 99° and boiling at 190° under 17 mm. pressure.

All these esters are only slightly soluble in water, but more or less soluble in organic solvents. Their aqueous solutions, when treated with barium hydroxide, yield the corresponding barium salts, whilst with ammonia or aniline, amides or anilides are obtained. N. L.

Hydroxymethylenecyanoacetic Esters. By E. Grégoire de Bollemont (*Bull. Soc. Chim.*, 1901, [iii], **25**, 28—38).—These compounds are readily obtained by treating the corresponding ethoxy- and methoxy-cyanoacrylates (see preceding abstract) with barium hydroxide and decomposing the barium salts thus obtained with sulphuric acid. The alkyl hydroxycyanoacrylates are strong acids, capable of displacing acetic acid from its salts, and readily estimated alkalimetrically. They are slightly soluble in water, but more soluble in alcohol or ether. The lower members of the series crystallise well; all undergo more or less decomposition when distilled under diminished pressure. Their aqueous solutions give an intense orange-brown coloration with ferric chloride.

Methyl hydroxymethylenecyanoacetate [*α-cyano-β-hydroxyacrylate*], $OH{\cdot}CH{:}C(CN){\cdot}CO_2Me$, has a pungent odour and melts at 136—137°. Determinations of the electric conductivity of the sodium salt at 25° gave a result $\mu_{1024-32} = 12{\cdot}01$, approaching the value (11·3) usually found for the salts of monobasic acids. The affinity coefficient (K 1·505) of the ester itself shows that it must be considered as a strong organic acid, occupying a position between chloroacetic and dichloroacetic acids. The *barium*, *copper*, and *silver* salts have been prepared and analysed; they are well crystallised compounds. The *ethyl* ester crystallises in colourless plates melting at 69° and has a less pronounced acid character than the preceding compound. The *barium* and *copper* salts have been prepared and analysed. The *amyl* ester could only be obtained in an impure state. The barium and silver salts of this ester have already been described (preceding abstracts). N. L.

Transformation of *O*-Acyl Derivatives of Ethyl Acetoacetate into the Isomeric *C*-Acyl Derivatives. By LUDWIG CLAISEN and E. HAASE (*Ber.*, 1900, **33**, 3778—3784).—Acetophenone acetal, $CH_3·CPh(OEt)_2$, can be converted into *iso*acetophenone ethyl ether, $CH_2:CPh·OEt$, and this is transformed into phenyl propyl ketone, $CH_2Et·CPhO$, when it is boiled under a pressure of two atmospheres (Abstr., 1897, i, 188). It has not been found possible in any way to effect a similar transformation with ethyl β-ethoxycrotonate (ethyl *O*-ethylacetoacetate), $CO_2Et·CH:CMe·OEt$. On the other hand, ethyl *O*-acetylacetoacetate, $CO_2Et·CH:CMe·OAc$, is converted into ethyl diacetoacetate, $CO_2Et·CHAc·CMeO$ or $CO_2Et·CHAc_2$, when it is dissolved in ethyl acetate (a little ethyl acetoacetate being added) and heated with potassium carbonate on the water-bath. A similar transformation can be effected with *methyl O-acetylacetoacetate,* which was prepared in like manner to the ethyl ester (Abstr. 1900, i, 373), boils at 95° under 17 mm. pressure, and has sp. gr. 1·1006 at 18°; the *copper* derivative of methyl diacetoacetate melts at 226—227°, and does not decompose from 200° onwards, as stated previously (Abstr., 1894, i, 32).

Without the addition of a little ethyl acetoacetate, the reaction takes place very slowly. The authors assume that even then a little of this substance is first formed, and then brings about the reaction described, first forming the potassio-derivative by means of the potassium carbonate present. "The transformation of the *O*-acetate by potassium carbonate into the potassium salt of the *C*-acetyl derivative is effected by means of a small quantity of ethyl potassioacetoacetate. The *O*-acetate reacts with this, forming ethyl potassiodiacetoacetate and ethylacetoacetate; and the regenerated ethyl acetoacetate reacts again as before." This view is borne out by the fact that ethyl sodioacetate and *O*-acetylacetate give a good yield of diacetoacetate when heated together on the water-bath. The transformation in question is analogous to that of sodium phenyl carbonate into sodium salicylate; such a migration of an acyl group from an O to a C atom is rare, however. Probably the formation of *C*-acyl derivatives of ethyl acetoacetate when the sodium derivative of this substance is treated with acid chlorides is to be explained, as a rule, in the same way, an *O*-acyl derivative being formed at first, and then undergoing transformation. C. F. B.

Decomposition of Normal Ammonium Oxalate. By HENRI GILLOT (*Bull. Acad. Roy. Belg.*, 1900, 744—767).—On boiling an aqueous solution of ammonium oxalate, the whole of the ammonia is progressively evolved, somewhat rapidly at first and more slowly later; in the case of a solution of 0·151 gram of the salt in 750 c.c. of water, elimination is complete after boiling for 15 hours, the source of heat being an oil-bath at 130—140°. The oxalic acid simultaneously undergoes partial decomposition into carbon dioxide and formic acid. At 70°, the decomposition of ammonium oxalate by water takes place very slowly, whilst at 50° it ceases altogether. Cold, dry air does not alter the composition of the hydrated salt, $(NH_4)_2C_2O_4,H_2O$; dry air at 65°, however, gradually expels the water of crystallisation, but not the ammonia; exposure of either the hydrated or anhydrous salt to moist air for $3\frac{1}{2}$ months at 19—22° yields a salt containing approximately $2\cdot7H_2O$ without ammonia being lost. This stability towards air is noteworthy, since most other ammonium salts, under similar conditions, lose a large part of their ammonia.

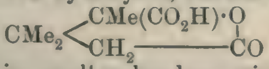
Aqueous solutions of ammonium oxalate evolve ammonia when exposed to light, the action being proportional to the intensity of illumination; thus, in bright sunlight after 46 days, 2·30 per cent. of the salt was decomposed; in diffused light, 0·85 per cent.; and in darkness, only 0·42 per cent. W. A. D.

Cineolic Acid. Resolution of *r*-Cineolic Acid into its Optically Active Components. By Hans Rupe and Max Ronus (*Ber.*, 1901, **33**, 3541—3546. Compare Abstr., 1900, i, 371).—Strychnine *d*-cineolate, $C_{31}H_{36}O_6N_2$, crystallises from hot water in large, compact prisms which melt at 195—197°. The mother liquors from this salt, on further evaporation, yield successively the salts of the inactive and lævo-acids.

d- and *l*-Cineolic acids separate from water in large, transparent crystals which melt at 79° and contain $1H_2O$. The anhydrous acids, obtained by exposure of the hydrated crystals in dry air, melt at 138—139°, and have $[\alpha]_D$ $+18\cdot56$ and $-19\cdot10$ respectively at 20° in aqueous solution. They are readily soluble in water, alcohol, or cold chloroform (unlike the racemic acid, which is sparingly soluble in chloroform); when crystallised from dry ethyl acetate or ether, they separate in the form of aggregated leaflets. The difference in solubility of the racemic and active acids in water is remarkable; the former dissolves in 133·3 parts of water at 8°, the latter in 11·2. The crystals of the *l*-acid belong to the rhombic system, $[a:b:c = 0\cdot9815:1:1\cdot4771]$.

It has been observed on more than one occasion that the active acids undergo auto-racemisation when crystallised, but no explanation of this is forthcoming. It was frequently observed, too, that on recrystallising the *d*-acid from water, an acid in the form of large plates or prisms, containing $1H_2O$ and melting at 123—126°, was formed, but after dehydration had the same melting point as the original acid.

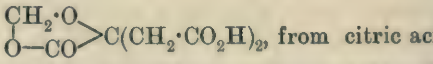
d-*Cineolic anhydride*, $C_{10}H_{14}O_4$, boils at 165—167° under 15 mm. pressure, dissolves sparingly in light petroleum, and crystallises from cold benzene in large, transparent, six-sided tablets melting at 108°. In benzene solution, it gave $[\alpha]_D$ $+45\cdot37$ at 20°. A. L.

Attempted Synthesis of $\alpha\beta\beta$-Trimethylglutaric Acid. By G. Blanc (*Bull. Soc. Chim.*, 1901, [iii], **25**, 68—73).—When $\beta\beta$-dimethyllævulic acid is treated with hydrocyanic acid, and the cyanohydrin thus produced is hydrolysed, the lactonic acid, *$\beta\beta\gamma$-trimethylpentane-$\alpha\gamma$-olidoic acid*,  $CMe_2<\begin{matrix}CMe(CO_2H)\cdot O\\ CH_2\text{————}CO\end{matrix}$, is obtained, which crystallises from water in small, colourless prisms melting at 163—164°. This acid has the same melting point as the isomeric lactonic acid,

$CMe_2<\begin{matrix}CH(CO_2H)\cdot O\\ CHMe\text{——}CO\end{matrix}$, which Balbiano (Abstr., 1900, i, 202) obtained by the oxidation of camphoric acid with potassium permanganate, but the two acids are essentially different, since a mixture of them melts between 110° and 120°. Moreover, the calcium and barium salts of the acid now described crystallise with 4 and $5H_2O$ respectively, whereas the corresponding salts of Balbiano's acid crystallise with 2 and $4H_2O$. Attempts to obtain αββ-trimethylglutaric acid by reducing the new lactonic acid with hydriodic acid were unsuccessful, however the experimental conditions were varied, although Balbiano's acid is stated to be readily reduced. This difference in the behaviour of the two acids is probably due to the fact that in the one the lactonic oxygen is connected with a tertiary carbon, and in the other to a secondary carbon atom. N. L.

New Formal (Methylene) Compounds of Hydroxy-acids. By William Alberda van Ekenstein (*Proc. K. Acad. Amst.*, 1900, 3, 400—403. Compare Weber and Tollens, Abstr., 1898, i, 61).—Formaldehyde reacts with certain hydroxy-acids in aqueous solution, and methylene derivatives are produced which differ from those already known, inasmuch as the carboxyl group takes part in the condensation. These compounds are obtained by the repeated evaporation of the solutions of the hydroxy-acids with excess of formaldehyde; the yield is small, and the product is separated from the unaltered material by extraction with ether, chloroform, or benzene.

The *compound*, $\begin{matrix}O\text{—}CO\\ CH_2\cdot O\end{matrix}>CH\cdot CH<\begin{matrix}CO\cdot O\\ O\text{—}CH_2\end{matrix}$, obtained from *d*-tartaric acid, crystallises in white needles, melts at 117°, and has $[\alpha]_D$ 112°; the substance has a neutral reaction and is hydrolysed by acids or alkalis. Mesotartaric acid yields a similar *compound* which melts at 106° and is inactive; racemic acid, however, does not interact with formaldehyde.

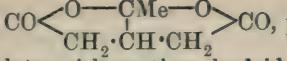


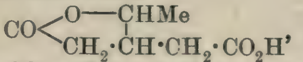
The *compound*, $\begin{matrix}CH_2\cdot O\\ O\text{—}CO\end{matrix}>C(CH_2\cdot CO_2H)_2$, from citric acid, melting at 200°, may be titrated in the cold as a dibasic acid. The oily *compound* obtained from malic acid contains one methylene group and is lævorotatory.

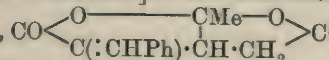
Formaldehyde has no action on salicylic and oxalic acids in aqueous solution, but it certainly reacts with the sugars, for their optical rotation is greatly affected, that of dextrose being doubled; the rotatory powers of galactose, lævulose, arabinose, and mannose are considerably decreased, whilst *d*-rhamnose becomes lævorotatory. The methylene compounds of these carbohydrates are very unstable and have not been isolated.

Benzaldehyde seems to interact with the sugars and hydroxy-acids in a similar manner, but the products are oily and unstable.

G. T. M.

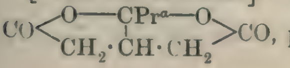
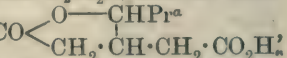
Dilactones. By Rudolph Fittig (*Annalen*, 1900, 314, 1—96. Compare Abstr., 1898, i, 11).—[With Ernst Roth]—The ketodilactone of β-acetylglutaric acid,  $\mathrm{CO}<\begin{array}{c}\mathrm{O{-}CMe{-}O}\\ \mathrm{CH_2\cdot CH\cdot CH_2}\end{array}>\mathrm{CO}$, prepared by heating dried sodium tricarballylate with acetic anhydride (1½ mols.) at 120—130° during 36 hours, melts at 99°, and is identical with the substance described by Emery (Abstr., 1897, i, 325); it is completely hydrolysed when boiled with water during 24 hours. According to Emery's statement, β-acetylglutaric acid melts at 47—50°, but the author has obtained it in aggregates of long leaflets melting at 58°; it is best prepared by converting the dilactone into the calcium salt, decomposing the aqueous solution with two-thirds the calculated quantity of hydrochloric acid, and allowing the ethereal extract to evaporate spontaneously. The *calcium* salt contains $3H_2O$, and the *silver* salt is anhydrous. The aniline derivative of the ketodilactone crystallises in leaflets and needles, and melts at 149°; according to Emery, the substance melts at 153—154°.

Valerolactoneacetic acid,  $\mathrm{CO}<\begin{array}{l}\mathrm{O{-}CHMe}\\ \mathrm{CH_2\cdot CH\cdot CH_2\cdot CO_2H}\end{array}$, prepared by reducing the ketodilactone with sodium amalgam, crystallises from chloroform in aggregates of small needles and melts at 84°; according to Emery, the substance melts at 78—79°. The *barium* salt is amorphous, and the *calcium* salt contains $2H_2O$. *Hydroxyethylglutaric acid*, $OH\cdot CHMe\cdot CH(CH_2\cdot CO_2H)_2$, arising from valerolactoneacetic acid on hydrolysis, has not been isolated, the lactone being regenerated very easily; the *barium*, *calcium*, and *silver* salts are anhydrous.

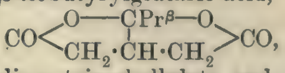
[With Wilhelm Sternberg].—The *ketodilactone* of benzylidene-β-acetylglutaric acid,  $\mathrm{CO}<\begin{array}{c}\mathrm{O{-}{-}{-}CMe{-}O}\\ \mathrm{C(:CHPh)\cdot CH\cdot CH_2}\end{array}>\mathrm{CO}$, obtained by heating dried sodium tricarballylate with acetic anhydride (1½ mols.) and benzaldehyde (1 mol.), crystallises in lustrous leaflets, and melts at 162°; the *dibromide*, $C_{14}H_{12}O_4Br_2$, crystallises from hot benzene in small needles, and melts and decomposes at 163°. *Benzylidene-β-acetylglutaric acid*, $C_{14}H_{14}O_5$, obtained by hydrolysing the dilactone, is converted into that substance so readily that it has not been isolated; the *calcium* salt contains $1\frac{1}{2}H_2O$, the *barium* salt $1H_2O$, and the *silver* salt is anhydrous.

When the ketodilactone of benzylidene-β-acetylglutaric acid is reduced with sodium amalgam, two isomeric substances, $C_{14}H_{14}O_4$, are produced. The *a-ketodilactone* crystallises from benzene and melts at 134°; hydrolysis converts it into a benzyl-β-glutaric acid, of which the *calcium* and *barium* salts contain $2H_2O$, whilst the *silver* salt is anhydrous. The *β-ketodilactone* crystallises from alcohol in stellate aggregates of leaflets, and melts at 169°; the *calcium* salt of the benzyl-β-glutaric acid, which it yields on hydrolysis, contains $2\frac{1}{2}H_2O$, the *barium* salt $4H_2O$, and the *silver* salt is anhydrous.

[With Ernst Roth].—The ketodilactone of benzylidene-β-acetylglutaric acid is also produced when dried sodium β-acetylglutarate is heated with benzaldehyde and acetic anhydride.

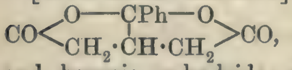
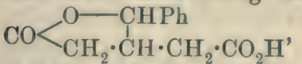
[With Tom Guthrie].—The *ketodilactone* of β-butyrylglutaric acid,  $\mathrm{CO}<\begin{array}{c}\mathrm{O{-}CPr^{a}{-}O}\\ \mathrm{CH_2\cdot CH\cdot CH_2}\end{array}>\mathrm{CO}$, produced on heating dried sodium tricarballylate with butyric anhydride at 125° during 12 hours, crystallises in needles on adding ether or petroleum to the solution in chloroform, and melts at 55°. *β-Butyrylglutaric acid,* $COPr^{\alpha}\cdot CH(CH_2\cdot CO_2H)_2$, crystallises in prisms or leaflets, and is readily soluble in water or alcohol; it melts at 88°, and belongs to the monoclinic system [$\beta = 58°30'$]. The *barium* salt contains $2H_2O$, the *calcium* salt $2\frac{1}{2}H_2O$, and the *silver* salt is anhydrous. *Heptolactoneacetic acid,*  $CO<\begin{matrix}O\text{——}CHPr^{\alpha}\\ CH_2\cdot CH\cdot CH_2\cdot CO_2H\end{matrix}$, formed when the ketodilactone is reduced with sodium amalgam, crystallises in rosettes of white needles and melts at 53°; the crystals belong to the monoclinic system [$a:b = 1\cdot5443:1$; $\beta = 78°56'$]. The *calcium* salt contains $2H_2O$, the *barium* and *silver* salts being anhydrous. Heptolactoneacetic acid is hydrolysed with difficulty, but the protracted action of concentrated barium hydroxide solution yields the dibasic acid, $C_9H_{16}O_5$, which could not be isolated; the *calcium*, *barium*, and *silver* salts are anhydrous.

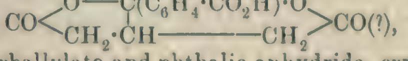
The *ketodilactone* of *β-iso*butyrylglutaric acid,

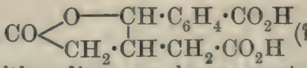


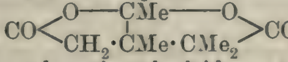
$$CO<\begin{matrix}O\text{——}CPr^{\beta}\text{—}O\\ CH_2\cdot CH\cdot CH_2\end{matrix}>CO,$$

prepared from dried sodium tricarballylate and *iso*butyric anhydride, melts at 89—90°. *β-*iso*Butyrylglutaric acid,* $COPr^{\beta}\cdot CH(CH_2\cdot CO_2H)_2$, melts at 99°, and crystallises in the monoclinic system [$a:b:c = 1\cdot5927:1:2\cdot5159$; $\beta = 81°6'$]. The *barium* salt contains $2H_2O$, and the *calcium* salt $3H_2O$, the *silver* salt being anhydrous.

[With HARRY SALOMON].—The *ketodilactone* of β-benzoylglutaric acid,  $CO<\begin{matrix}O\text{——}CPh\text{—}O\\ CH_2\cdot CH\cdot CH_2\end{matrix}>CO$, obtained from dried sodium tricarballylate and benzoic anhydride, melts at 137°, and separates, on adding ether to the chloroform solution, in rhombic crystals [$a:b:c = 0\cdot6478:1:0\cdot8659$]. *β-Benzoylglutaric acid,* $COPh\cdot CH(CH_2\cdot CO_2H)_2$, crystallising from a mixture of ether and petroleum in bundles of needles, melts at 122°; the *barium* salt contains $4H_2O$, the *calcium* and *silver* salts being anhydrous. *Phenylbutyrolacetoneacetic acid,*  $CO<\begin{matrix}O\text{——}CHPh\\ CH_2\cdot CH\cdot CH_2\cdot CO_2H\end{matrix}$, prepared by reducing the dilactone with sodium amalgam, crystallises from water in transparent prisms and melts at 114°; the *barium* salt contains $3H_2O$, and the *calcium* salt $2H_2O$, the *silver* salt being anhydrous. Phenylbutyrolactoneacetic acid is hydrolysed only slowly, and the dibasic hydroxy-acid, $C_{12}H_{14}O_5$, could not be isolated; the *calcium* and *barium* salts contain $1H_2O$, and the *silver* salt is anhydrous. When dried phenylbutyrolactoneacetic acid is distilled, β-methylphenyl*iso*crotonic acid and β-methylnaphthol are produced.

[With OSKAR GOTTSCHE].—The *ketodilactone* of β-phthaloylglutaric acid,  $CO<\begin{matrix}O\text{——}C(C_6H_4\cdot CO_2H)\cdot O\\ CH_2\cdot CH\text{————}CH_2\end{matrix}>CO(?)$, prepared from dried sodium tricarballylate and phthalic anhydride, crystallises from chloroform in colourless needles, and melts at 208°. *β-Phthaloylglutaric acid,* $CO_2H\cdot C_6H_4\cdot CO\cdot CH(CH_2\cdot CO_2H)_2$, produced by the action of boiling water on the dilactone, crystallises from ether in small needles, but has no definite melting point, undergoing a change at 135—140°, and finally becoming liquid at the melting point of the dilactone; the *calcium* salt contains $5H_2O$, the *barium* salt $9H_2O$, and the *silver* salt is anhydrous.

Carboxyphenylbutyrolactoneacetic acid,  $CO{<}\begin{array}{l}O{-}CH\cdot C_6H_4\cdot CO_2H\\ CH_2\cdot CH\cdot CH_2\cdot CO_2H\end{array}$ (?), obtained by reducing the ketodilactone with sodium amalgam, crystallises from boiling water in lustrous plates containing $1H_2O$, which is removed at 100°; acetone also deposits it in monoclinic plates, and when anhydrous it melts at 165°. The *calcium* salt contains $2H_2O$, and the *barium* salt $6H_2O$, the *silver* salt being anhydrous. Hydrolysis with alkalis proceeds slowly, and the dibasic hydroxy-acid, $C_{13}H_{14}O_7$, has not been isolated; the *barium* and *calcium* salts contain $10H_2O$, whilst the *silver* salt is anhydrous.

[With HARRY SALOMON].—The *ketodilactone* of β-acetyltrimethylglutaric acid,  $CO{<}\begin{array}{l}O{-}CMe{-}O\\ CH_2\cdot CMe\cdot CMe_2\end{array}{>}CO$, obtained from dried sodium camphoronate and acetic anhydride, crystallises from chloroform in long needles, and melts at 147·5—148°. *β-Acetyltrimethylglutaric acid,* $CO_2H\cdot CH_2\cdot CMe(COMe)\cdot CMe_2\cdot CO_2H$, crystallises from boiling water in prisms, softens at 125°, and melts at 140°; the *barium* salt contains $3\frac{1}{2}H_2O$, the *calcium* salt $2H_2O$, and the *silver* salt is anhydrous. The acid resists the action of sodium amalgam. M. O. F.

Syntheses with Ethyl Sodioacetoacetate and the Formation of Rings of Four Carbon Atoms by means of Sodium Ethoxide. By ARTHUR MICHAEL (*Ber.*, 1900, **33**, 3731—3769).—The ester of a substituted malonic acid was mixed with a solution of sodium in absolute alcohol, and the ester of an unsaturated acid was added; the whole was sometimes warmed to complete the reaction. The alcohol was distilled off, the residue dissolved in ether, and substances of an acid nature removed by shaking with dilute aqueous potassium hydroxide; of these acid substances, a part could be set free by saturating the alkaline liquid with carbon dioxide. The neutral product of the reaction was thus obtained pure; other observers (Auwers, Abstr., 1891, i, 546; 1892, i, 41; Ruhemann and Cunnington, Trans., 1898, **73**, 1006) have omitted the extraction of the acid products, and obtained only mixtures of different substances.

Ethyl ethylmalonate and fumarate give ethyl pentane-αβγγ-tetracarboxylate, $CO_2Et\cdot CH_2\cdot CH(CO_2Et)\cdot CEt(CO_2Et)_2$, which boils at 197° (corr.) under 13·5 mm. pressure; the ethyltricarballylic acid obtained from it by hydrolysis melts at 155—157°. Of the acid products, one is soluble in aqueous alkali carbonate, and appears to be the triethyl hydrogen ester, for at 180° it loses carbon dioxide and forms a liquid that boils at 168—169° under 11 mm. pressure and has the composition of ethyl pentane-αβγ-tricarboxylate. Sodium dissolves in an ethereal solution of the tetrethyl salt, and when the product is freed from ether and heated with methyl iodide at 100°, *ethyl α-methylpentane-αβγγ-tetracarboxylate* is obtained; this boils at 201—202° (corr.) under 12 mm. pressure, is acted on further by sodium in ethereal solution.

and when hydrolysed with boiling, dilute hydrochloric acid, yields a product melting at 138—146° after several recrystallisations, presumably a mixture of stereoisomeric methylethyltricarballylic acids.

Ethyl methylmalonate and fumarate give ethyl butane-αβγγ-tetracarboxylate. This boils at 206·5—207° (corr.) under 20 mm. pressure; when hydrolysed, it yields only β-methyltricarballylic acid melting at 143—146°, and not a mixture of stereoisomerides. Sodium acts on it, and the product reacts at 100° with methyl iodide to form *ethyl α-methylbutane-αβγγ-tetracarboxylate*; this boils at 198—199° under 13 mm. pressure, reacts further with sodium, and can be hydrolysed, although with difficulty, to *α-methylbutane-αβγ-tricarboxylic acid*, which melts at 190—193°; probably a little of the stereoisomeric acid is formed at the same time.

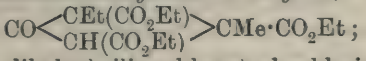
Ethyl malonate and citraconate give *ethyl β-methylpropane-αβγγ-tetracarboxylate.* This boils at 199—199·5° (corr.) under 11 mm. pressure, and can be hydrolysed, although with difficulty, to β-methyltricarballylic acid melting at 168—173°. From its sodium derivative and methyl iodide, *ethyl β-methylbutane-αβγγ-tetracarboxylate* can be obtained; this boils at 202—203° (corr.) under 13 mm. pressure, is attacked slowly by sodium, and can be hydrolysed, although with difficulty, to a mixture of stereoisomeric *β-methylbutane-αβγ-tricarboxylic acids*, from which a product melting at 196—198° was obtained by repeated recrystallisation. By using ethyl instead of methyl iodide, *ethyl β-methylpentane-αβγγ-tetracarboxylate* is obtained; this boils at 199—200° (corr.) under 10 mm. pressure, can be hydrolysed slowly, and reacts further with sodium. When the sodium derivative of ethyl β-methylpropane-αβγγ-tetracarboxylate is treated with water, the solution freed from neutral substances by extraction with ether, and saturated with carbon dioxide, ethyl methylketotetramethylenetricarboxylate is formed; the sodium derivative of ethyl β-methylpentane-αβγγ-tetracarboxylate yields an analogous ketotetramethylene derivative (see below).

Ethyl methylmalonate and crotonate give *β-methylbutane-αγγ-tricarboxylate*; this boils at 160·5—161° (corr.) under 10 mm. pressure, and reacts readily with sodium; the product of this reaction, when heated with methyl iodide, yields *ethyl dimethylbutane-αγγ-tricarboxylate*, boiling at 161—162° (corr.) under 9 mm. pressure.

Ethyl malonate and crotonate give ethyl β-methylpropane-αγγ-tricarboxylate, boiling at 165—166° (corr.) under 11 mm. pressure, together with a little ethyl βδ-dimethylpentane-αγγε-tetracarboxylate, boiling and decomposing slightly at 204—207° (corr.) under 9 mm. pressure; the second product must have resulted from the condensation of the first with ethyl crotonate. The sodium derivative of ethyl β-methylpropane-αγγ-tricarboxylate reacts with methyl iodide; the resulting *methyl* derivative boils at 166—167° (corr.) under 10 mm. pressure, and reacts only slowly with sodium; it is not identical with the ethyl β-methylbutane-αγγ-tricarboxylate described above.

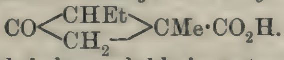
Ethyl propane-αββ-tricarboxylate (from ethyl ethenyltricarboxylate, sodium ethoxide, and methyl iodide) appears to form a little of a sodium derivative, but only with great difficulty.

Ethyl ethylmalonate and citraconate yield hardly any of the normal condensation product. The chief product is soluble in alkali hydroxides, but is liberated by saturation with carbon dioxide; it boils at 204—205° (corr.) under 13 mm. pressure, and yields an *oxime*, *phenylhydrazone* and *semicarbazone*, all oily in consistency. It was identified as *ethyl methylethylketotetramethylenetricarboxylate*,



$$\mathrm{CO}{<}\begin{matrix}\mathrm{CEt(CO_2Et)}\\ \mathrm{CH(CO_2Et)}\end{matrix}{>}\mathrm{CMe{\cdot}CO_2Et};$$

it is hydrolysed readily by boiling dilute hydrochloric acid to a mixture of isomeric *methylethylketotetramethylenecarboxylic acids*,



$$\mathrm{CO}{<}\begin{matrix}\mathrm{CHEt}\\ \mathrm{CH_2}\end{matrix}{>}\mathrm{CMe{\cdot}CO_2H}.$$

Of these, the one which is less soluble in water melts at 72—74°; its *silver* salt and *semicarbazone* (melting at 193—194°) were analysed; the more soluble one melts at 37—39°, its *semicarbazone* at 191—192°; when distilled (at 180—182° under 15 mm. pressure) or heated in aqueous solution, it undergoes a partial transformation into the less soluble isomeride.

Ethyl methylmalonate and citraconate yield *ethyl dimethylketotetramethylenetricarboxylate*, boiling at 207—208° (corr.) under 20 mm. pressure. When hydrolysed, this yields a mixture of isomeric *dimethylketotetramethylenecarboxylic acids*, which boils at 187° (corr.) under 25 mm. pressure, and melts at 56—59°; the *semicarbazone* melts at 195—196°.

Ethyl malonate and citraconate yield, in addition to the product described above, *ethyl methylketotetramethylenetricarboxylate*, boiling at 213—214° (corr.) under 17 mm. pressure. When hydrolysed, this yields a single *methylketotetramethylenecarboxylic acid*, melting at 62—64°; the *semicarbazone* melts at 192—193°.

When ethyl cinnamate in ethereal solution is digested with sodium until the latter has dissolved, the product poured into water, and the aqueous solution extracted with ether, an oil boiling at 205—210° under 15—17 mm. pressure is obtained, probably a product of polymerisation. From ethyl crotonate, a product was obtained boiling at 126° (corr.) under 9 mm., at 258—259° under 773 mm. pressure. It has a composition and vapour density corresponding to a bimolecular polymeride of the ester, $C_{12}H_{20}O_4$. When hydrolysed, it yields a dibasic *acid*, $C_8H_{12}O_4$, which melts at 128—129°, and is oxidised almost instantly by permanganate; its *silver* and *barium* salts, the latter with $1H_2O$, were prepared and analysed.

In an introduction to the paper, the mechanism of the reactions described is considered from the point of view occupied by the author (Abstr., 1900, i, 321). C. F. B.

Action of Formaldehyde Solution on Calcium Carbide. By Ludwig Vanino (*Chem. Centr.*, 1900, ii, 1150; from *Pharm. Centr.-H.*, 1900, 41, 666).—Formaldehyde may be used to moderate the action of water on calcium carbide. With a solution of formalin in 8 vols. of water, the rate of evolution of acetylene is much slower than with water, whilst in 40 per cent. solution the aldehyde almost completely inhibits the action. E. W. W.

Specific Difference between Ketones and Aldehydes. By William Oechsner de Coninck and Servant (*Bull. Acad. Roy. Belg.*, 1900, 313—316).—Whereas ketones, either alone or in presence of water or dilute alkali, are not changed at the ordinary temperature by the long-continued passage through them of a current of air, aldehydes under the same conditions are sensibly oxidised to acids; the experiments were made with acetone, benzophenone, and acetaldehyde.

W. A. D.

Methyl Ethyl Ketone. By Léon Van Reymenant (*Bull. Soc. Roy. Belg.*, 1900, 724—744).—The product of the action of chlorine (1 mol.), or of sulphuryl chloride on methyl ethyl ketone, consists, two-thirds of the secondary chloro-derivative, COMe·CHMeCl (Vladesco, Abstr., 1892, 424, 810), and nearly one-third of *chloromethyl ethyl ketone*, $CH_2Cl·CO·CH_2Me$. The former boils at 115° under 758 mm. pressure, has a sp. gr. 1·032 at 0°, and, on oxidation, yields α-chloropropionic acid; the latter boils at 125° under 756 mm. pressure, has a sp. gr. 1·08 at 13°, n_D 1·42701 at 10°, a mol. refraction 25·35 (calc. 25·55), and yields chloroacetic acid on oxidation. With bromine, similar *derivatives*, COMe·CHMeBr and $CH_2Br·CO·CH_2Me$, are obtained, the former boiling at 133—134°, and the latter at 145—146°; both are nearly colourless, tear-exciting liquids, which become coloured in the light. *β-Acetylethyl acetate*, $CH_3·CO_2·CHMeAc$, obtained by boiling the foregoing secondary chloro-derivative with alcoholic potassium acetate, boils at 164° under the ordinary pressure, has a sp. gr. 1·027 at 13°, n_D 1·4143 at 13·5°, and a mol. refraction 31·62 (calc. 31·61); *propionylmethyl acetate*, $CH_3·CO_2·CH_2COEt$, corresponding with the primary chloro-derivative, boils at 176°, and has a sp. gr. 1·029 at 13·4°, n_D 1·4151, and a mol. refraction 31·37 (calc. 31·37). *Methylacetylcarbinol*, CHMeAc·OH, obtained by hydrolysing either the corresponding chloro-derivative or acetate, melts at 15°, boils at 148°, and has a sp. gr. 1·012 at 16·5°, n_D 1·4272, and a mol. refraction 22·20 (calc. 23·32). *Propionylcarbinol*, $OH·CH_2·CO·CH_2Me$, boils at 160°.

Although cyanoacetone, $CH_2Ac·CN$, cannot be obtained by the interaction of chloroacetone with potassium cyanide, the latter readily converts the foregoing halogen derivatives of methyl ethyl ketone into their cyanides at the ordinary temperature. *α-Acetylpropionitrile*, CHMeAc·CN, boils at 145—146° (Vladesco, *loc. cit.*, gives 156°), has a sp. gr. 1·494 at 13°, and a mol. refraction 25·03 (calc. 25·33); with sodium ethoxide, it forms a *sodium* derivative, CNaMeAc·CN, which, with methyl iodide, yields *dimethylacetylacetonitrile*, $CMe_2Ac·CN$, a yellow liquid which boils at 163—164°, and has a sp. gr. 1·008 at 13°. The sodium derivative reacts with chlorine, forming *α-chloro-α-acetylpropionitrile*, CClMeAc·CN, a yellowish liquid boiling at 95° under 45 mm. pressure; the analogous *bromo*-derivative, CBrMeAc·CN, boils at 122° under 30 mm. pressure. Both these compounds react energetically with potassium cyanide to form *methylacetylmalononitrile*, $CMeAc(CN)_2$, which boils at 195°.

α-Acetylpropionic acid, $CHMeAc·CO_2H$, obtained by hydrolysing its nitrile, boils at 224° under 34 mm. pressure. *a-Chloro-a-acetylpropionic acid*, $CClMeAc \cdot CO_2H$, boils at 141° under 45 mm. pressure, and *a-bromo-a-acetylpropionic acid*, $CBrMeAc \cdot CO_2H$, at 150° under the same pressure.

Propionylacetonitrile, $COEt \cdot CH_2 \cdot CN$, obtained from the corresponding chloro-derivative, boils at 164°, has a sp. gr. 0·976 at 9°, and a mol. refraction 25·00 (calc. 27·03). W. A. D.

Derivatives of Methyl Nonyl Ketone. By Henri Carette (*Compt. rend.*, 1900, **131**, 1225—1227).—Methyl nonyl ketone and benzaldehyde do not interact even at 120° unless they are mixed together in the presence of potassium hydroxide. The *compound*, $C_{18}H_{26}O$, produced when a cold 0·25 per cent. solution of the alkali in dilute alcohol is added to a mixture of the ketone and aldehyde in mol. proportions, readily dissolves in the ordinary organic solvents, melts at 41—42°, and boils at 245° under 35 mm. pressure. The *polymeride*, $(C_{18}H_{26}O)_2$, obtained either by boiling the preceding compound with a 1 per cent. solution of potassium hydroxide in 95 per cent. alcohol, or by heating its generators in the same medium, crystallises in needles, melts at 116°, and boils with partial decomposition at 310—340° under 35 mm. pressure. G. T. M.

Birotation of Dextrose. By Yukichi Osaka (*Zeit. physikal. Chem.*, 1900, **35**, 661—706).—The change of rotation of dextrose takes place in accordance with the equation $k = 1/t.\log_e(a_0 - a_0)/(a - a_0)$, where a_0 and a_0 are the initial and final rotations, and a is the rotation at the time t. This has been proved by Levy (Abstr., 1895, i, 586) and Trey (Abstr., 1896, ii, 139; 1897, ii, 299), and the author now finds, using numbers obtained by Tollens and others, that the same law holds in the case of lævulose, rhamnose, *l*-arabinose, fucose, *l*-xylose, *d*-galactose, maltose, and milk sugar. In the case of dextrose, the change of rotation is accelerated in the presence both of hydroxyl and hydrogen ions, the catalytic effect of the former, however, being much greater than that of the latter. The velocity of the retrogression of the rotation is approximately proportional to the concentration of the hydroxyl ions, and to the square root of the concentration of the hydrogen ions. Neutral salts appear to increase the catalytic efficiency of the hydroxyl ions, but to be practically without effect on that of the hydrogen ions. The author agrees with Cohen (Abstr., 1900, ii, 716) in regarding dextrose as a very weak acid. J. C. P.

Influence of the Nature and Intensity of Light on the Inversion of Sucrose by Mineral Acids. By Henri Gillot (*Bull. Acad. Roy. Belg.*, 1900, 863—874).—The author has examined comparatively the rate of inversion of sucrose in aqueous solution containing sulphuric or hydrochloric acid, when exposed to light of different wave-lengths; in each case, the fall of rotatory power and the increase of cupric-reducing power were compared with similar values obtained with a solution left in darkness. Light of all wave-lengths promotes inversion, but rays in the blue, violet, and ultra-violet are much more active than those in the yellow or red. W. A. D.

Behaviour of Sucrose Solutions towards Strontia at 125—128°. By A. SCHÖNE and BERNHARD TOLLENS (*Zeit. Ver. deut. Zucker-Ind.*, 1900, 978—979).—When aqueous solutions of sucrose and strontium hydroxide are heated together in an autoclave at 125—128°, no trace of raffinose is formed. The raffinose present in molasses hence comes from the beet. T. H. P.

Diagnosis of Primary and Secondary Amines. By OSCAR HINSBERG (*Ber.*, 1900, **33**, 3526—3529. Compare Abstr., 1891, 49).—Solonina (*J. Russ. Phys. Chem. Soc.*, 1897, **29**, 404; Abstr., 1900, i, 147) and Bamberger (Abstr., 1899, i, 701) have shown that benzene- or toluene-sulphonic chloride cannot always be used with success in the diagnosis of primary and secondary amines. The author now recommends β-anthraquinonesulphonic chloride in the presence of excess of alkali (MacHoul, Abstr., 1881, 51). The amide thus obtained, if discoloured, is recrystallised and then 0·05 gram dissolved in hot alcohol, and to the colourless, or only pale yellow, solution, 0·5 c.c. of 25 per cent. potassium hydroxide is added. If a secondary amine were originally present, the colour remains unaltered, and on addition of more alkali, the sulphonamide is precipitated in a crystalline form; with a primary amine, however, the solution assumes a deep yellow or yellowish-red colour owing to the formation of a salt. The method has been tried with a number of bases and has given very satisfactory results.

*β-Anthraquinonesulphone-*n*-heptylamide*, $C_{14}H_7O_2 \cdot SO_2 \cdot NH \cdot C_7H_{15}$, forms yellow needles melting at 160° and insoluble in water.

β-Anthraquinonesulphonemethylanilide, $C_{14}H_7O_2 \cdot SO_2 \cdot NMePh$, forms pale yellow needles melting at 182°. J. J. S.

Alternation of Volatility in the Series of Normal Primary Diamines. By LOUIS HENRY (*Bull. Acad. Roy. Belg.*, 1900, 795—803).—In the series of normal primary monoamines, $NH_2 \cdot CH_2 \cdot [CH_2]_n \cdot CH_3$, there is a regular progressive increase in the boiling point of about 27°, the difference between the boiling points of the even pair, C_2 and C_4 (57°), being practically the same as that of the odd pair, C_3 and C_5 (54°). In the case of the diamines, $NH_2 \cdot [CH_2]_n \cdot NH_2$, however, there is an alternation in boiling point similar to that traced in the case of the acid chlorides (Abstr., 1899, i, 735), the successive differences in boiling point of the C_2, C_3, C_4, and C_5 diamines being 19°, 25°, and 19°. The difference between the even pair, C_2 and C_4 (44°), is, however, the same as that between the odd pair, C_3 and C_5 (44°). Similar relationships connect the boiling points of the two classes of amines and those of the parent hydrocarbons; for these, the original should be consulted. W. A. D.

Action of α-Chlorohydrin on some Tertiary Amines. By ALEXANDER BIENENTHAL (*Ber.*, 1900, **33**, 3500—3506).—The *additive* compound, $NEt_3Cl \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH$, formed on heating α-chlorohydrin with triethylamine for 8 hours at 100°, is a non-crystallisable syrup which, when treated with moist silver hydroxide in aqueous solution, yields a strongly caustic *base*; the *picrate* of the latter forms long prisms melting at 114°, and the *platinichloride* monoclinic plates melting at 215·5°.

The *additive* compound, $NPr_3Cl\cdot CH_2\cdot CH(OH)\cdot CH\cdot OH$, of tripropylamine, obtained similarly, is also a syrup; the *picrate* of the *base*, $OH\cdot NPr_3\cdot C_3H_7O_2$, crystallises from alcohol in small, yellow prisms, and melts at 79—80°, the *aurichloride* melting at 94—95°.

The *compound*, $C_5NH_{10}MeCl\cdot C_3H_7O_2$, formed by the interaction of 1-methylpiperidine and α-chlorohydrin at 100°, crystallises from alcohol in long prisms, sinters at 229° and melts at 233—234°; the *platinichloride* of the derived *base* crystallises from alcohol in thick, yellow prisms, and decomposes at 206—207°, the crystalline *mercurichloride* melting at 169—170°.

The *compound*, $C_9NH_7Cl\cdot C_3H_7O_2$, derived from quinoline, crystallises from alcohol in small, white leaflets, melts at 170°, and, with moist silver oxide, yields a *base* the *platinichloride* of which forms small, yellow plates melting at 282—283°; the *aurichloride* is amorphous and melts at 100—101°, the *mercurichloride* forms transparent, white needles melting at 114—115°, and the *picrate* melts at 120°.

The *strychnine* derivative, $C_{21}H_{22}O_2N_2Cl\cdot C_3H_7O_2$,, formed on heating the components for 1 hour at 190°, crystallises from alcohol in white prisms, and does not melt at 290°; it is not acted on by alkalis, but with moist silver oxide yields a *base* the *platinichloride* of which crystallises from alcohol in small, yellow needles melting at 230°; the *aurichloride* melts at 214°, and the *mercurichloride* at 199°, whilst the *picrate* decomposes at 280°.

No well-characterised derivative could be obtained by the interaction of 2-picoline with α-chlorohydrin. W. A. D.

Conversion of Amino-fatty Acids into the Corresponding Chloro-acids.

By Emil Jochem (*Zeit. physiol. Chem.*, 1900, **31**, 119—131. Compare Curtius, Abstr., 1884, 42; Tilden, Trans., 1895, **67**, 489).—Chlorinated acids are readily obtained when 1 mol. proportion of sodium nitrite in concentrated solution is added drop by drop to the amino-acid dissolved or suspended in 10 times its weight of concentrated hydrochloric acid. The method has given good results with amino-derivatives of the acetic and oxalic acid series, also with aromatic-amino acids which contain the amino-group in a side chain, but not when the amino-group is directly attached to the benzene nucleus, or yet with fatty or aromatic amines.

This reaction accounts for the formation of chloro-acids when albumin is treated with hydrochloric acid and sodium nitrite.

α-Chloroglutaric acid, $C_5H_7O_4Cl$, crystallises from a mixture of ether and light petroleum in well developed pyramids, sinters at 97°, and is completely melted at 100°; it dissolves readily in most solvents, with the exception of benzene, chloroform, or light petroleum; aqueous solutions of the acid or of its salts readily decompose, yielding α-hydroxyglutaric acid. The *copper* and *barium* salts are both readily soluble in water, but are precipitated on the addition of alcohol; the *diethyl* ester is an oil distilling at 140—145° under 15 mm. pressure, and has a sp. gr. 1·14 at 23°.

α-Chloroisohexoic acid, $C_6H_{11}O_2Cl$, has been obtained from leucine in the form of an oil insoluble in water, and readily undergoes decomposition, evolving hydrogen chloride even at 40°; its *ethyl* ester distils at 190° under atmospheric, or at 91—95° under 15 mm., pressure, and has a sp. gr. 1·01 at 23°; when hydrolysed, it yields an α-hydroxy*iso*hexoic acid melting at 67—70°, the zinc salt of which contains $2H_2O$ (compare Waage, *Annalen*, 1861, **118**, 87; Gmelin, Abstr., 1894, i, 501). J. J. S.

Action of Pyruvic Acid on its Ammonium Salt. By A. W. K. de Jong (*Rec. Trav. Chim.*, 1900, **19**, 259—310).—The pyruvic acid employed was prepared by a modification of the methods devised by Visser (here described for the first time) and Simon, namely, by heating together potassium hydrogen tartrate, potassium hydrogen sulphate, and sulphuric acid. The estimation of the acid is effected by means of its phenylhydrazone, and the corrections necessary for the solubility of the compound are given.

When solid ammonium carbonate is gradually added to a concentrated solution of pyruvic acid, a considerable elevation of temperature occurs, carbon dioxide is evolved, and *ammonium α-acetylaminopropionate* slowly crystallises out. Estimation of the amount of carbon dioxide evolved shows that for each mol. of the latter a mol. of ammonia enters into reaction. The free acid is obtained by adding to pyruvic acid half the quantity of ammonium carbonate required for neutralisation, or by treating the ammonium salt with an equivalent quantity of pyruvic acid. α-Acetylaminopropionic acid, $NHAc\cdot CHMe\cdot CO_2H$, crystallises in large, rhombic plates or needles $[a : b : c = 0{\cdot}7729 : 1 : 1{\cdot}0983]$, melts at 132—133°, and is soluble in water or alcohol but almost insoluble in ether. When heated with hydrochloric acid or sodium hydroxide solution, it is hydrolysed to acetic acid and α-alanine. Conversely, α-acetylaminopropionic acid is readily obtained by heating α-alanine with a slight excess of acetic anhydride at about 70°. The following metallic salts of α-acetylaminopropionic acid have been prepared; the sodium and potassium salts could only be obtained as hygroscopic syrups, the others are crystalline: ammonium with H_2O, barium with $1\frac{1}{2}H_2O$, calcium with $1\frac{1}{2}H_2O$, magnesium with $7H_2O$, zinc with H_2O, lead with $3H_2O$, copper, and silver with H_2O.

Ethyl α-acetylaminopropionate crystallises in hygroscopic needles melting at 39—40°, and by the action of chlorine is converted into the corresponding *chloroethyl* ester, $C_5H_8O_3N\cdot CHClMe$, which, on hydrolysis, yields hydrogen chloride, acetaldehyde, and α-acetylaminopropionic acid. The *amide*, $C_5H_8O_3N\cdot NH_2$, crystallises in small, rhombic prisms melting at 157—158°.

α-Acetylaminopropionic acid also forms salts with acids. The *hydrochloride*, $C_5H_9O_3N,HCl$, crystallises in hygroscopic needles and is unstable. The *nitrate* crystallises in very soluble needles melting and decomposing at 64—65°. When neutralised with calcium carbonate, the well-crystallised double salt, $(C_5H_8O_3N)_2Ca,(NO_3)_2Ca,6H_2O$, is formed.

Ammonium pyruvate, when pure, forms white needles. As an explanation of the formation of α-acetylaminopropionic acid, it is suggested that ammonium pyruvate is tautomeric with the as yet unknown *a*-aminohydroxypropionic acid. On this hypothesis, the reactions concerned in the formation of *a*-acetylaminopropionic acid are brought into harmony with the views generally held as to the action of ammonia on aldehydes and ketones.

From the mother liquors obtained in the preparation of *a*-acetylaminopropionic acid, two new acids of the composition $C_6H_{11}O_5N$ have been isolated by means of their barium salts. The one crystallises in needles decomposing at 220°, whilst the other crystallises, with $1H_2O$, in small prisms which decompose at 208°. The barium and silver salts of these acids have been prepared and analysed. N. L.

Action of Ammonia and Aniline on Hydroxymethylenecyanoacetic Esters and their Alkyl Derivatives. By E. GRÉGOIRE DE BOLLEMONT (*Bull. Soc. Chim.*, 1901, [iii], **25**, 39—46).—The alkyl hydroxy-, methoxy-, and ethoxy-cyanoacrylates (this vol., i, 116), when treated with ammonia, yield one and the same series of amino-derivatives, $NH_2\cdot CH\colon C(CN)\cdot CO_2R$. These are stable, crystalline compounds which are very slightly soluble in water, but soluble in alcohol, ether, or excess of ammonia; their solutions are neutral, and give no coloration with ferric chloride.

Methyl aminomethylenecyanoacetate [*β-amino-a-cyanoacrylate*],

$$NH_2\cdot CH\colon C(CN)\cdot CO_2Me,$$

crystallises in long, colourless needles melting at 128°. The *ethyl* ester crystallises in slender needles melting at 130° and boiling at 216° under 19 mm. pressure. The *propyl* ester crystallises in small prisms melting at 46°, and the *amyl* ester in large, white scales melting at 101°.

The following anilino-derivatives are precisely analogous to these amino-derivatives.

Ethyl anilinomethylenecyanoacetate [*β-anilino-a-cyanoacrylate*],

$$NHPh\cdot CH\colon C(CN)\cdot CO_2Et,$$

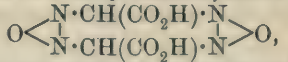
crystallises from alcohol in long needles or thin, monoclinic plates, according to the temperature and concentration. The *methyl* ester crystallises in slender, white needles melting at 175°, the *propyl* ester in large tablets melting at 89—90°, and the *amyl* ester in white scales melting at 90°. N. L.

Constitution of Nitroferricyanides. By ARTURO MIOLATI (*Zeit. anorg. Chem.*, 1900, **25**, 318).—A question of priority (compare Hofmann, Abstr., 1900, i, 591). E. C. R.

Physico-chemical Researches on the Behaviour of Uric Acid and its Salts in Solution. By WILHELM HIS, jun., and THEODOR PAUL (*Zeit. physiol. Chem.*, 1900, **31**, 1—42, and 64—78. Compare Abstr., 1900, i, 591).—The authors review previous work on the solubility of uric acid, and they find that 1 part of the acid is soluble in 39,480 parts of water at 18°. When the finely divided acid is shaken with water at 18°, a saturated solution is obtained in an hour; it is not permissible to cool a solution saturated at a high temperature, on account of decomposition of the uric acid. The molecular conductivity of a saturated uric acid solution is 32·24 at 18°, when allowance has been made for the conductivity of the solvent water. Indirectly, by work on sodium and potassium urate solutions, it is found that the molecular conductivity of uric acid for infinite dilution is 339 at 18°. Hence, in a saturated uric acid solution, 9·5 per cent. of the acid is electrolytically dissociated. Further, the affinity constant has the value 0·00000151. The authors confirm the observation made by other workers, that uric acid is decomposed on prolonged contact with water, this leading to an increased solubility. A saturated solution of uric acid in contact with platinised electrodes is more rapidly decomposed, and its conductivity diminishes.

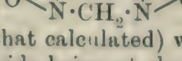
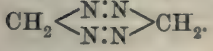
As regards the solubility of uric acid in solutions of mineral acids, theory requires a repression of the dissociation and consequent diminution of the solubility. This conclusion is borne out both qualitatively and quantitatively by experiment: 1 part of uric acid dissolves in 42,430 parts of *N*-hydrochloric acid and in 44,140 parts of *N*-sulphuric acid. Even in more concentrated acid solutions, the solubility is less than in pure water, whence it follows that uric acid cannot act as a base. The tendency of uric acid to decompose when in contact with water practically disappears in the presence of mineral acids. The estimation of uric acid in urates by precipitation with excess of hydrochloric, or, better, sulphuric acid is an exact process; a correction of 2 mg. for each 100 c.c. of liquid at 18° should be applied. J. C. P.

Bisazoxyacetic Acid, Bisazoxymethane, and Hydraziacetic Acid. By ARTHUR HANTZSCH and MARTIN LEHMANN (*Ber.*, 1900, 33, 3668—3685).—The substance described by Curtius (Abstr., 1889, 369) as triazoxyacetic acid is in reality bisazoxyacetic acid,



$$O<\begin{array}{l}N\cdot CH(CO_2H)\cdot N\\ \mid \qquad\qquad\qquad\quad \mid \\ N\cdot CH(CO_2H)\cdot N\end{array}>O,$$

and is best prepared by exposing powdered bisdiazoacetic acid to the gas evolved from nitric acid and arsenious oxide, although it is also formed by the action of bromine vapour and chlorine on the acid. It is a purple-red powder, which forms a carmine-red solution in water, and decomposes at 148° evolving purple vapours of bisazoxymethane. It is quantitatively reduced in aqueous solution at 0° by hydrogen sulphide to bisdiazoacetic acid. The aqueous solution of the acid rapidly decomposes and becomes colourless, hydraziacetic acid being formed. The solution in 1 mol. of sodium hydroxide also rapidly decomposes, whilst the solution of the normal sodium salt is quite stable. This salt, $C_2H_2O_2N_4(CO_2Na)_2$, crystallises in flat, hygroscopic, red plates. The *barium* salt is a heavy, orange-yellow, microcrystalline powder, and the *silver* salt is a dark green powder which explodes very violently at 210°. The silver salt reacts with alkyl iodides, but the resulting esters could only be obtained in the form of impure, viscid oils.

Bisazoxymethane,  $O<\begin{array}{l}N\cdot CH_2\cdot N\\ \mid \qquad\quad\; \mid \\ N\cdot CH_2\cdot N\end{array}>O$, is formed in very small amount (1—2 per cent. of that calculated) when bisazoxyacetic acid is gently heated, carbon dioxide being at the same time formed and a residue of impure bisdiazomethane left. It is obtained pure by sublimation, in delicate, purple-red needles often 1 centimetre in length, and when quickly heated melts at 75°. It dissolves in water and many organic solvents, and decomposes when preserved. In benzene solution, the molecular weight determined by the cryoscopic method agrees with that required for the formula just given. On reduction with hydrogen sulphide in aqueous solution, it is converted into bisdiazomethane,  $CH_2{<}\begin{matrix}N{:}N\\N{:}N\end{matrix}{>}CH_2$.

Hydraziacetic acid, $\begin{matrix}NH\\|\\NH\end{matrix}{>}CH{\cdot}CO_2H$, is formed from bisazoxyacetic acid according to the equation $C_4H_4O_6N_4 = C_2H_4O_2N_2 + 2CO_2 + N_2$, when the aqueous solution of the latter is allowed to decompose at 25—30°. It is a very sparingly soluble, crystalline powder, and decomposes at 190°. It has a conductivity μ 73 (at 25° and v 32), and is, therefore, as strong an acid as monochloroacetic acid, and forms stable soluble salts. The *methyl* ester, prepared from the silver salt, crystallises in small needles melting at 102°, and has the calculated molecular weight in benzene solution. It is readily soluble in water, and when treated in this solution with mercuric oxide yields methyl diazoacetate. Hydraziacetic acid decomposes when its solution is boiled, or when it is treated with acids, into hydrazine and glyoxylic acid, and the latter then undergoes a secondary reaction, yielding oxalic and glycollic acids. Both bisdiazoacetic acid and bisazoxyacetic acid are converted by alkaline reduction into hydraziacetic acid. A. H.

New Reactions of Organometallic Derivatives. By EDMOND E. BLAISE (*Compt. rend.*, 1901, **132**, 38—41).—The author has investigated the reactions between nitriles, alkyl haloids, alkyl salts of the α-bromo-acids of the acetic series, and alkylcarbimides in presence of magnesium bromide or iodide, or zinc bromide. In the case of nitriles, the reaction is $R{\cdot}C{:}N + MgBrR' = RR'C{:}N{\cdot}MgBr$ and the imino-derivatives thus obtained yield ketones, $R{\cdot}CO{\cdot}R'$, on treatment with dilute acids. The condensation of nitriles of the benzene series with alkyl iodides in presence of magnesium yields new ketones and also the corresponding semicarbazones, the *o*-nitriles reacting less readily than the *p*-nitriles. Nitriles of the acetic series likewise yield ketones when treated with the organo-metallic derivatives.

With the alkyl salts of α-bromo-acids of the acetic series the reaction is $R{:}CN + Zn + CR'HBr{\cdot}CO_2Et = ZnBr{\cdot}N{:}CR{\cdot}CHR'{\cdot}CO_2Et$, and the products yield alkyl salts of the β-ketonic acids, $R{\cdot}CO{\cdot}CHR'{\cdot}CO_2Et$. This method is of very general application, since the radicles may be varied in both the nitrile and the bromo-acid. With ethyl bromoacetate, however, the condensation goes further, but this difficulty is got over by condensing ethyl cyanoacetate with alkyl iodides in presence of magnesium, $CN{\cdot}CH_2{\cdot}CO_2Et + EtMgI = CO_2Et{\cdot}CH_2{\cdot}CEt{:}N{\cdot}MgI$ and, subsequently, $CO_2Et{\cdot}CH_2{\cdot}COEt$. No other general method admits of the preparation of the alkyl salts of the acylacetic acids.

With dinitriles, the reaction is $CN{\cdot}CN + EtMgI = CN{\cdot}CEt{:}N{\cdot}MgI$ and $CN{\cdot}CEt{:}N{\cdot}MgI + EtMgI = MgI{\cdot}CN + CEt_2{:}N{\cdot}MgI$, a ketone being obtained from this product in the usual way. With carbimides, the reaction is $NPh{:}C{:}O + RMgI = NPh{:}CR{\cdot}O{\cdot}MgI$ and subsequently $NPh{:}CR{\cdot}OH$ and $NHPh{\cdot}CO{\cdot}R$. Other similar reactions are under investigation. Caprylene, hexylene, and phenylacetylene do not condense with organo-metallic derivatives under the usual conditions.

C. H. B.

Electrolytic Oxidation of Toluene. By AARON MERZBACHER and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1900, **22**, 723—725).—The electrolytic oxidation of toluene has already been attempted (see James, Abstr., 1899, i, 909). The authors have varied the conditions and succeeded in obtaining a small quantity of benzaldehyde and ethyl benzoate at the anode. The anode liquid was an alcoholic solution of toluene, and the cathode liquid was a sulphuric acid solution. Similar results have been obtained with ethylbenzene in place of toluene.

J. C. P.

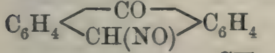
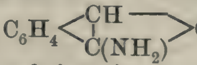
Phenyl-*p*-nitro-*o*-tolylsulphone and some of its Derivatives. By R. S. NORRIS (*Amer. Chem. J.*, 1900, **24**, 469—491).—*p*-Nitro-*o*-toluenesulphonic chloride crystallises in large, yellow rhombs, and melts at 44°. When this compound is heated with benzene in presence of aluminium chloride, *phenyl-*p*-nitro-*o*-tolylsulphone*, $NO_2\cdot C_6H_3Me\cdot SO_2Ph$, is obtained which crystallises from hot alcohol in thin plates, melts at 158°, and is easily soluble in benzene, acetone, or hot light petroleum. The sulphone dissolves in concentrated sulphuric and nitric acids and is reprecipitated on dilution with water; when treated with fuming sulphuric acid, it is converted into a sulphonic acid, $C_{13}H_{11}O_7NS_2$, the *barium* salt of which was prepared and analysed. Sodium and potassium hydroxides react with the sulphone with formation of a purple precipitate.

*Phenyl-*p*-amino-*o*-tolylsulphone*, $NH_2\cdot C_6H_3Me\cdot SO_2Ph$, obtained by reducing phenyl-*p*-nitro-*o*-tolylsulphone with ammonium sulphide, crystallises from alcohol in thin plates, melts at 156°, and dissolves readily in alcohol, acetone, or benzene.

Phenyl-*p*-nitro-*o*-tolylsulphone is not attacked by chromic acid, but when treated with aqueous potassium permanganate, it is converted into p-*nitro*-o-*phenylsulphonebenzoic acid*, $NO_2\cdot C_6H_3(SO_2Ph)\cdot CO_2H$, which crystallises in white needles, melts at 196°, and is easily soluble in acetone; its *barium* and *calcium* salts are described. This acid is isomeric with the *p*-nitro-*o*-benzoylbenzenesulphonic acid obtained by Hollis (Abstr., 1900, i, 293). Phosphorus pentachloride readily reacts with the acid with production of p-*nitro*-o-*phenolsulphonebenzoic chloride*, which separates from chloroform in colourless, rhombic crystals, melts at 109°, and dissolves easily in chloroform, ether, benzene, or light petroleum; it is not affected by water at the ordinary temperature, but is readily decomposed by hot water or dilute alkali hydroxides. By the action of dilute ammonia, the chloride is converted into p-*nitro*-o-*phenylsulphonebenzamide*, which crystallises from chloroform in prisms, melts at 191—192°, and is readily soluble in acetone or hot alcohol. On the addition of aluminium chloride to a warm solution of *p*-nitro-*o*-phenylsulphonebenzoic chloride in benzene, a brown, tarry mass was obtained which was not further investigated.

With a view to obtaining *p*-nitro-*o*-cyanodiphenylsulphone which, on hydrolysis, would yield *p*-nitro-*o*-phenylsulphonebenzoic acid, a solution of *p*-nitro-*o*-cyanobenzenesulphonic chloride in benzene was heated with aluminium chloride, but only a tarry product was obtained from which *p*-nitro-*o*-cyanodiphenylsulphone could not be isolated. E. G.

Systematisation and Nomenclature of Dicyclic Compounds. By ADOLF VON BAEYER (*Ber.*, 1900, **33**, 3771—3775).—The paper constitutes an attempt to systematise the nomenclature of compounds derived from those dicyclic hydrocarbons which contain two or more atoms of carbon common to both rings. M. O. F.

Nitroanthracene. By JACOB MEISENHEIMER (*Ber.*, 1901, **33**, 3547—3549).—Liebermann and Lindemann's "nitrosoanthrone,"  $C_6H_4<\begin{smallmatrix}CO\\CH(NO)\end{smallmatrix}>C_6H_4$ (Abstr., 1881, 99) is in reality 10-*nitroanthracene*, $C_6H_4<\begin{smallmatrix}CH\\|\\C(NO_2)\end{smallmatrix}>C_6H_4$, as it is not identical with anthraquinonemonoxime. On reduction with stannous chloride, it is converted into 10-anthramine,  $C_6H_4<\begin{smallmatrix}CH\\|\\C(NH_2)\end{smallmatrix}>C_6H_4$, which for complete identification was converted into its *acetyl* derivative, $C_{16}H_{13}ON$. This separates from alcohol in greenish needles melting at 273—274°, and in alcoholic solution shows a beautiful blue fluorescence. A. L.

Compounds of Metallic Salts with Aromatic Amines. By DANIEL TOMBECK (*Ann. Chim. Phys.*, 1900, [vii], **21**, 383—419).—This paper contains a detailed account of the preparation and properties of the compounds from metallic salts and organic amines; the majority of these substances have already been described (compare Abstr., 1897, i, 463, 560; 1898, i, 566). Aniline and its homologues form compounds with silver oxy-salts, two mols. of the base combining with one of the metallic sulphate or nitrate. These substances dissolve in cold water without alteration, but decompose when their solutions are warmed, producing silver mirrors on the walls of the containing vessels. Ethylaniline unites with silver nitrate to form a compound of this type, but does not combine with other oxy-salts.

The three anhydrous calcium halogen salts combine with two molecular proportions of aniline, forming deliquescent compounds separating in tabular crystals. G. T. M.

Electrolytic Reduction of Nitro-compounds. By ALBERT ROHDE (*Zeit. Elektrochem.*, 1900, **7**, 328—332, and 338—341).—The experiments were made by the method of Elbs (Abstr., 1899, i, 270; this vol., i, 74).

m-Nitrodimethylaniline gives tetramethyl-*m*-diaminoazobenzene; yield 93 per cent. Further reduction yields the hydrazo-compound.

*Dimethyl-*m*-nitro-*o*-toluidine*, ($Me:NMe_2:NO_2 = 1:2:4$), was prepared by nitration of dimethyl-*o*-toluidine dissolved in a large excess of concentrated sulphuric acid, in the cold, the yield being 91 per cent. of the calculated quantity. The compound is a yellowish oil which, when reduced electrolytically, yields tetramethyl-*m*-diamino-*p*-azotoluene; yield 86 per cent. By recrystallisation from alcohol, it is obtained in leaflets melting at 99°. Further reduction leads to the hydrazo-compound, which forms colourless crystals melting at 127°. When exposed to the air, this is oxidised to the azo-compound, which, however, appears to be a different modification, since it crystallises in more needle-shaped crystals, and melts at 119°. The hydrazo-compound did not yield a benzidine derivative.

m-Nitromethylaniline gives, on reduction, dimethyl-*m*-diaminoazobenzene, in yield of about 85 per cent. Further reduction gives a solution of the hydrazo-compound, which was not isolated in the solid form.

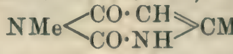
p-Nitrodimethylaniline gives dimethylamine, and *p*-aminophenol, when reduced in a hot solution in the usual way; in the cold, *p*-aminodimethylaniline is formed. An azo- or hydrazo-compound was not formed in either case. These results are readily explained on the assumption that a phenylhydroxylamine derivative, $OH{\cdot}NH{\cdot}C_6H_4{\cdot}NMe_2$, is first formed, which undergoes intermolecular change, yielding a diiminoquinone, $NH{:}C_6H_4{:}NMe_2{\cdot}OH$. In the hot liquid, this compound decomposes into dimethylamine and $NH{:}C_6H_4{:}O$, from which *p*-aminophenol is derived, whereas in the cold solution it is reduced without decomposition to *p*-aminodimethylaniline.

Benzoyl-*p*-nitrodiphenylamine yields *p*-azoxybenzoyldiphenylamine when the solution is not allowed to become too strongly alkaline; the substance forms yellow leaflets and melts at 178°. Further reduction gives the corresponding azo-compound, melting at 172°.

p-Nitrodiphenylamine gives *p*-aminodiphenylamine in yield of 70 per cent.

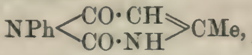
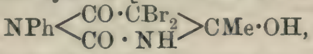
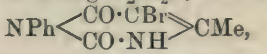
o- and *p*-Nitroanilines yield 70 per cent. and 86 per cent. respectively of the theoretical quantity of *o*- and *p*-phenylenediamine.

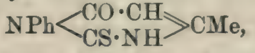
1-Nitro-2-ethoxynaphthalene yields 1-amino-2-ethoxynaphthalene. If, however, the reduction is carried out in a solution of ammonium acetate instead of sodium acetate, a comparatively small quantity of an azoxy-compound is obtained as intermediate product. T. E.

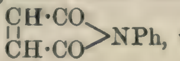
Ethyl β Aminocrotonate. By ROBERT BEHREND, FERDINAND C. MEYER, and YNGVE BUCHHOLZ (*Annalen*, 1900, **314**, 200—230. Compare Behrend and Dietrich, Abstr., 1900, i, 120).—Although it has been supposed that the formula  $NMe<\begin{matrix}CO{\cdot}CH\\CO{\cdot}NH\end{matrix}>CMe$ expresses the constitution of α-dimethyluracil as well as of the β-modification (*loc cit.*), it is now found that the structure of the former substance is represented by the expression $NH<\begin{matrix}CO{-}CH\\CO{\cdot}NMe\end{matrix}>CMe$. In the course of this investigation, the existence of two ethyl β-aminocrotonates was revealed (Behrend, Abstr., 1899, i, 331, and Knoevenagel, *ibid.*, 478). The labile ester melts at 20°, and separates from light petroleum in large, prismatic crystals belonging to the monoclinic system $[a:b:c = 0{\cdot}97:1:?;\ \beta = 53{\cdot}5°]$. The stable form, melting at 33°, crystallises in the same system $[a:b:c = 1{\cdot}0111:1:1{\cdot}2108;\ \beta = 88°\ 27'\ 14'']$.

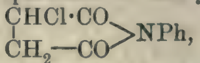
Ethyl iminoacetylmalonoanilate, $NH{:}CMe{\cdot}CH(CO_2Et){\cdot}CO{\cdot}NHPh$, obtained in association with ethyl phenyluraminocrotonate when phenylcarbimide acts on ethyl β-aminocrotonate, crystallises from alcohol in needles, and melts at 125—126°; the crystals belong to the monoclinic system [$a:b:c = 1{\cdot}627:1:1{\cdot}045$; $\beta = 78°0'$]. Alcoholic potassium hydroxide resolves the substance into aniline, ammonia, carbon dioxide, acetic acid, and acetylacetanilide; concentrated hydrochloric acid gives rise to aniline, ammonia, and carbon dioxide, whilst concentrated sulphuric acid converts it into ethyl acetylmalonoanilate.

Ethyl phenyluraminocrotonate, $\mathrm{NHPh{\cdot}CO{\cdot}NH{\cdot}CMe{:}CH{\cdot}CO_2Et}$, crystallises from light petroleum in broad needles, and melts at 98—99°; concentrated hydrochloric acid resolves it into carbon dioxide, aniline, and ammonia.

Phenylmethyluracil,  $\mathrm{NPh}<\begin{matrix}\mathrm{CO{\cdot}CH}\\ \mathrm{CO{\cdot}NH}\end{matrix}>\mathrm{CMe}$, prepared by heating ethyl phenyluraminocrotonate with alkali hydroxides, melts at 244—245°, and crystallises from hot water in microscopic, six-sided leaflets belonging to the monoclinic system [$a:b:c = 1{\cdot}41:1:?$] *Dibromohydroxyphenylmethyluracil*,  $\mathrm{NPh}<\begin{matrix}\mathrm{CO{\cdot}CBr_2}\\ \mathrm{CO{\cdot}NH}\end{matrix}>\mathrm{CMe{\cdot}OH}$, obtained by the action of bromine on finely divided phenylmethyluracil suspended in water, is an amorphous substance containing $1\frac{1}{2}H_2O$, and decomposes at 190°. *Bromophenylmethyluracil*,  $\mathrm{NPh}<\begin{matrix}\mathrm{CO{\cdot}CBr}\\ \mathrm{CO{\cdot}NH}\end{matrix}>\mathrm{CMe}$, produced when dibromohydroxyphenylmethyluracil is heated with alcohol in a reflux apparatus, crystallises in nacreous leaflets, and melts at 241—242°, when it becomes brown.

Ethyliminoacetylmalonothionanilate, $\mathrm{NH{:}CMe{\cdot}CH(CO_2Et){\cdot}CS{\cdot}NHPh}$, prepared from ethyl β-aminocrotonate and phenylthiocarbimide, melts at 135—136°, and crystallises from dilute alcohol in yellow prisms belonging to the monoclinic system [$a:b:c = 1{\cdot}463:1:1{\cdot}040$; $\beta = 76°34'$]. *Thionphenylmethyluracil*,  $\mathrm{NPh}<\begin{matrix}\mathrm{CO{\cdot}CH}\\ \mathrm{CS{\cdot}NH}\end{matrix}>\mathrm{CMe}$, melts at 253—255°, and crystallises from hot dilute alcohol in colourless, six-sided leaflets belonging to the monoclinic system [$a:b:c = 1{\cdot}45:1:?$]. When heated with concentrated hydrochloric acid at 170° during 5 hours, it yields hydrogen sulphide and phenylmethyluracil. M. O. F.

Maleanilide. By WILLEM A. VAN DORP and P. M. VAN HAARST (*Rec. Trav. Chim.*, 1900, 19, 311—317).—When malephenylamic acid, $\mathrm{CO_2H{\cdot}CH{:}CH{\cdot}CO{\cdot}NHPh}$, is heated at 100° with phosphorus oxychloride, a *compound*, $C_{16}H_{15}O_4N_2Cl_2P$, is produced, which crystallises in yellow needles, decomposes when heated at 145°, and is decomposed by water with the formation of hydrochloric and phosphoric acids and of nearly the theoretical quantity of *maleanilide*, $\mathrm{C_2H_2(CO{\cdot}NHPh)_2}$. Maleanilide crystallises in prisms melting at 175—180°, and is insoluble in water, but more or less soluble in organic solvents. The *hydrochloride*, $C_{16}H_4O_2N_2,HCl$, crystallises in yellow needles which decompose when heated to about 160°; it is also decomposed by cold water, and when boiled with methyl alcohol is converted into maleanil,  $\begin{matrix}\mathrm{CH{\cdot}CO}\\ \| \\ \mathrm{CH{\cdot}CO}\end{matrix}>\mathrm{NPh}$, with elimination of aniline hydrochloride. When fused, maleanilide is converted into the isomeric fumaranilide, which crystallises in needles melting at 312°.

From the mother liquors obtained in the preparation of the yellow compound, $C_{16}H_{15}O_4N_2Cl_2P$, *chlorosuccinanil*,  $\left.\begin{array}{l}\mathrm{CHCl{\cdot}CO}\\ \mathrm{CH_2{-}CO}\end{array}\right>\mathrm{NPh}$, was isolated; it crystallises in colourless needles melting at 118—119°.

N. L.

Action of Nitrosoacylamines on Primary Bases. By H. Apitzsch (*Ber.*, 1900, **33**, 3521—3525. Compare Abstr., 1899, i, 268).—When nitrosobenzoylbenzylamine (Abstr., 1899, i, 134) (1 mol.) and aniline (2 mols.) are heated together, first very gently and finally on the water-bath, until the evolution of nitrogen ceases, the products are benzanilide, benzylaniline, a little benzoic acid, and oily neutral substances. With *p*-toluidine, the products are *p*-benzotoluidide melting at 156—158°, and *benzyl*-p-*toluidine*, which was isolated in the form of *benzyltolylbenzenesulphonamide*, $CH_2Ph{\cdot}N(C_6H_4Me){\cdot}SO_2Ph$; this crystallises in long, colourless needles melting at 123—124°.

Nitrosobenzoylbenzylamine and phenylhydrazine yield *s*-benzoylphenylhydrazine (Fischer, Abstr., 1878, 308), and probably benzylphenylhydrazine, but this could not be isolated.

J. J. S.

Two Dinitromethyl-*p*-toluidines. By Johannes Pinnow [and in part Richard Mayer] (*J. pr. Chem.*, 1900, [ii], **62**, 505—522. Compare Abstr., 1897, i, 338).—When β-dinitromethyl-*p*-toluidine is reduced with ammonium sulphide, it is converted into 5-*nitromethyltolylene*-2 : 4-*diamine*, [$Me:NH_2:NHMe:NO_2 = 1:2:4:5$], which crystallises in long, lustrous brown leaflets, melts at 168°, and dissolves easily in acetone, ethyl acetate, glacial acetic acid, hot alcohol, chloroform, or hot benzene. The *acetyl* derivative crystallises in yellowish-brown prisms or needles, melts at 205·5—207°, and is soluble in most organic solvents, but only sparingly so in cold benzene, ether, or hot water. By the action of amyl nitrite on a solution of nitromethyltolylene-2 : 4-diamine in pyridine, *dinitrodiaminodimethyldiazoaminotoluene* is obtained in small, yellow prisms of the composition $3C_{16}H_{19}O_4N_7,2C_5H_5N$; this substance melts and decomposes at 267·5°, is fairly soluble in hot pyridine or nitrobenzene, and, when heated, loses its pyridine of crystallisation; if reduced with zinc dust in neutral solution, it is converted into methyl-2 : 4 : 5-triaminotoluene.

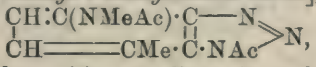
When β-dinitromethyl-*p*-toluidine is reduced with zinc and hydrochloric acid, a mixture of γ-diamino-*p*-toluidine and diaminomethylcresol is produced; these substances may be separated by means of their acetyl derivatives. *Triacetylmethyl*-2 : 4 : 5-*triaminotoluene* crystallises in rhombic prisms, melts and decomposes at 257—258°, and is fairly soluble in hot water or hot alcohol. *Diacetylmethyldiaminocresol* crystallises in slender needles containing $1H_2O$, which it loses slowly at 115—125°; it melts at 151—152°, and dissolves easily in hot alcohol.

Diacetylmethyltolylene-2 : 4-*diamine*, obtained by the action of acetic anhydride on methyl-*p*-tolylenediamine, crystallises in prisms, melts at 183—184°, and dissolves readily in the usual organic solvents when hot, but less readily in the cold; when heated with hydrochloric acid, trimethylbenziminazole is produced.

Acetyl-β-dinitromethyltoluidine, prepared by the addition of sulphuric acid to a hot solution of 2 : 3-dinitromethyl-*p*-toluidine in acetic anhydride, crystallises from alcohol or pyridine in bright yellow needles, melts at 151°, and dissolves readily in acetone, chloroform, glacial acetic acid, benzene, hot alcohol, or ethyl acetate.

Nitromethyltolylenediamine, obtained by the reduction of 2 : 3-dinitromethyl-*p*-toluidine with alcoholic ammonium sulphide, crystallises in lustrous, nearly black prisms, melts at 127—128°, and is very easily soluble in chloroform, methyl alcohol, or hot benzene.

*Methyl-*2 : 3 : 4-*triaminotoluene hydrochloride,* obtained by reducing 2 : 3-dinitromethyl-*p*-toluidine with zinc and hydrochloric acid, crystallises in double truncated pyramids, and melts and decomposes at 161—171°; by the action of acetic anhydride, it is converted into *diacetylmethyl-*2 : 3 : 4-*triaminotoluene,* which crystallises in needles or prisms, melts at 198—198·5°, and is soluble in alcohol, chloroform, glacial acetic acid, acetone, ethyl acetate, benzene, or water. When diacetylmethyl-2 : 3 : 4-triaminotoluene is heated with glacial acetic acid, 4-*acetylamino-*1 : 2 : 5-*trimethylbenzimidazole* is produced, which crystallises in needles, melts at 217—218°, and dissolves easily in alcohol or glacial acetic acid. By the action of nitrous acid on diacetylmethyltriaminotoluene, *diacetylmethylaziminotoluene* [4-*acetylmethylamino-*1-*acetyl-*7-*methylbenzotriazole*],



$$\left.\begin{array}{l}\mathrm{CH{:}C(NMeAc){\cdot}C{-\!\!-}N}\\ \mathrm{CH{=\!=\!=}CMe{\cdot}C{\cdot}NAc}\end{array}\right>\mathrm{N},$$

is obtained in slender, white needles; it melts at 169°, and is fairly soluble in alcohol and sparingly so in benzene, ether, or water.

Benzoyl-γ-dinitromethyltoluidine crystallises from alcohol in prisms and melts at 110·5°.

Acetyl-γ-dinitromethyltoluidine crystallises in slender, yellow needles, melts at 90·5°, and is soluble in most organic solvents; when reduced with zinc and hydrochloric acid, a *substance* is produced which crystallises in rhombic prisms, melts and decomposes at 222·5°, and appears to consist of a mixture of $C_{10}H_{13}O_2N_3,xH_2O$ and $C_{10}H_{12}O_2N_3Cl,xH_2O$.

E. G.

***p*- and *o*-Toluidinoacetic Acid and *a*-*p*- and *a*-*o*-Toluidinopropionic Acid.** By FRIEDRICH STEPPES (*J. pr. Chem.*, 1900, [ii], 62, 481—504).—The principal product of the action of monochloroacetic acid on *p*-toluidine is not *p*-toluidinoacetic acid (*p*-tolylglycine), as stated by Meyer (Abstr., 1896, i, 401) and by Schwebel (Abstr., 1878, 302), but a *substance* which melts at 174°, and is the *p*-toluidine salt of an acid; this acid, however, could not be isolated, on account of its instability. A small quantity of *p*-toluidinoacetic acid is produced; it melts at 120—121°, and is identical with the acid obtained by Meyer (*loc. cit.*) by the hydrolysis of its ethyl ester, and also with that prepared by Sieber (Abstr., 1899, i, 128) from the corresponding nitrile.

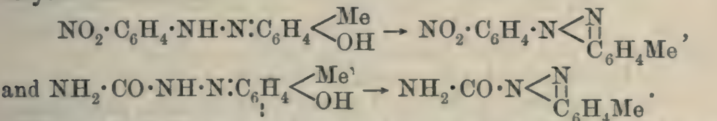
When monochloroacetic acid reacts with *o*-toluidine, a nearly quantitative yield of *o*-toluidinoacetic acid is obtained, as previously shown by Staats (Abstr., 1880, 387). If *o*-toluidine is treated with hydrocyanic acid, and the mixture added to a solution of formaldehyde (40 per cent.), o-*toluidinoacetonitrile* is obtained as a thick, uncrystallisable oil; it is converted by concentrated sulphuric acid into o-*toluidinoacetamide*, which crystallises in needles, melts at 140°, is easily soluble in hot water or alcohol, fairly so in warm benzene, and sparingly in ether, and on hydrolysis yields *o*-toluidinoacetic acid.

By the action of *a*-bromopropionic acid on *p*-toluidine, *a*-*p*-toluidinopropionic acid is produced almost quantitatively; it crystallises in pearly leaflets, melts at 158°, and is identical with the acid obtained by Tiemann and Stephan (Abstr., 1883, 199) from the corresponding nitrile.

a-*o*-Toluidinopropionic acid may be prepared by the action of *a*-bromopropionic acid on *o*-toluidine; it crystallises in colourless needles, melts at 118°, and dissolves readily in glacial acetic acid, alcohol, ether, or hot water. When an ethereal solution of *o*-toluidine and hydrocyanic acid is added to acetaldehyde, small, colourless needles, melting at 80—81°, and plates or prisms, melting at 96°, are produced in approximately equal quantities; the former are soluble in 20 per cent. hydrochloric acid, whilst the latter are insoluble. Both these substances yield *a*-*o*-toluidinopropionamide when dissolved in strong sulphuric acid; if the acid solution of the plates is poured into water, acetaldehyde is produced, but this does not occur in the case of the needles. The needles consist of *a*-*o*-toluidinoacetonitrile, whilst the plates have the composition: C, 74·73; H, 6·90; N, 19·33 per cent. The amide corresponds in its characters with that described by Tiemann and Stephan (*loc. cit.*), and on hydrolysis yields *a*-*o*-toluidinopropionic acid. E. G.

Mechanism of the Conversion of Arylhydroxylamines into Aminophenols. By EUGEN BAMBERGER (*Ber.*, 1900, **33**, 3600—3622). —By the action of sulphuric acid, or of alum-solution, or occasionally by the action of water alone, on arylhydroxylamines, a *p*-aminophenol is usually produced, but when the para-position is occupied by a halogen, *o*-aminophenols are produced, and these occasionally appear even when the para-position is occupied by hydrogen; *p*-aminophenolsulphonic acids are occasionally formed, and ethyl- or methyl-alcoholic sulphuric acid gives rise to derivatives of *p*- or *o*-phenetidine or anisidine; other occasional products are *p*-aminodiphenylamine bases, *p*-hydroxydiphenylamines, quinols (the hydroxy-groups sometimes causing a methyl group to wander from the para- to the meta-position), resorcinol ethers, and polymeric benzylenimines.

These facts are explained by the assumption that water is first split off, $C_6H_5\cdot NH\cdot OH \rightarrow C_6H_5\cdot N\!<$, and that the product, if methylated in the para-position, may then pass into a benzylenimine, $Me\cdot C_6H_4\cdot N\!< \rightarrow CH_2{:}C_6H_4{:}NH$, but usually recombines with water to an 'iminoquinol' [imino-ψ-quinol], $NH{:}C_6H_4\!<^{H}_{OH}$; this usually passes directly into a *p*-aminophenol, $NH_2\cdot C_6H_4\cdot OH$, but may be etherified to $\mathrm{NH{:}C_6H_4}{<}\begin{smallmatrix}\mathrm{H}\\ \mathrm{OR}\end{smallmatrix}$, or hydrolysed to $\mathrm{O{:}C_6H_4}{<}\begin{smallmatrix}\mathrm{H}\\ \mathrm{OH}\end{smallmatrix}$, or converted into a sulphate, $\mathrm{NH{:}C_6H_4}{<}\begin{smallmatrix}\mathrm{H}\\ \mathrm{O\cdot SO_3H}\end{smallmatrix}$, and thus give rise, by further isomeric change, to anisidines, phenetidines, quinols, and sulphonic acids. In the case of the para-methylated hydroxylamines, a number of the intermediate products can be isolated, although this has not been found possible in other cases, owing to the rapidity with which the changes occur. The 'iminoquinols' [imino-ψ-quinols] cannot be isolated, although they can be shown to be present, as they rapidly hydrolyse to the 'quinol' [ψ-quinol], $\mathrm{O{:}C_6H_4}{<}\begin{smallmatrix}\mathrm{CH_3}\\ \mathrm{OH}\end{smallmatrix}$, the constitution of which is proved by reduction to the phenol $\mathrm{HO\cdot C_6H_4Me}$, and isomeric change to the bivalent phenol, $\mathrm{HO\cdot C_6H_3Me\cdot OH}$; in presence of alcoholic sulphuric acid, the reversion to the true benzene structure takes place in two directions, by the wandering of the methyl group, $\mathrm{O{:}C_6H_4}{<}\begin{smallmatrix}\mathrm{CH_3}\\ \mathrm{OH}\end{smallmatrix} \rightarrow \mathrm{OH\cdot C_6H_3Me\cdot OEt}\,[=1:3:4]$, or by the wandering of the hydroxyl group, $\mathrm{O{:}C_6H_4}{<}\begin{smallmatrix}\mathrm{CH_3}\\ \mathrm{OH}\end{smallmatrix} \rightarrow \mathrm{OEt\cdot C_6H_3Me\cdot OEt}\,[=1:4:3]$. By the action of *p*-nitrophenylhydrazine or of semicarbazide, the 'quinols' [ψ-quinols] are converted into hydrazones or semicarbazones, which cannot be isolated, as they immediately lose water and give dicyclic derivatives:



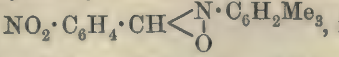
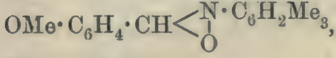
$$\mathrm{NO_2\cdot C_6H_4\cdot NH\cdot N{:}C_6H_4}{<}\begin{smallmatrix}\mathrm{Me}\\ \mathrm{OH}\end{smallmatrix} \rightarrow \mathrm{NO_2\cdot C_6H_4\cdot N}{<}\begin{smallmatrix}\mathrm{N}\\ \|\\ \mathrm{C_6H_4Me}\end{smallmatrix},$$

$$\text{and } \mathrm{NH_2\cdot CO\cdot NH\cdot N{:}C_6H_4}{<}\begin{smallmatrix}\mathrm{Me}\\ \mathrm{OH}\end{smallmatrix} \rightarrow \mathrm{NH_2\cdot CO\cdot N}{<}\begin{smallmatrix}\mathrm{N}\\ \|\\ \mathrm{C_6H_4Me}\end{smallmatrix}.$$

The 'quinols' [ψ-quinols] are analogous to the alkali-insoluble oxidation products of the phenols and phenol-bromides (Auwers, Abstr., 1900, i, 161). T. M. L.

Mesitylhydroxylamine and Nitrosomesitylene. By EUGEN BAMBERGER and ADOLF RISING (*Ber.*, 1901, 33, 3623—3636).—Mesitylhydroxylamine, $\mathrm{C_6H_2Me_3\cdot NH\cdot OH}$, melts at 116°, and when quite pure can be kept in closed vessels for 3 weeks without decomposition, but usually changes into a mixture of nitrosomesitylene and mesidine, together with nitromesitylene and azomesitylene, which are probably formed from the preceding compounds; a similar decomposition is brought about by air-free solutions of sodium hydroxide, whilst water and dilute sulphuric acid give, in addition, a small amount of trimethyl-ψ-quinol, $\mathrm{O{:}C_6H_2Me_3\cdot OH}$ (see the following abstracts).

Phenylmesitylhydroxycarbamide, $\mathrm{NHPh\cdot CO\cdot N(OH)\cdot C_6H_2Me_3}$, prepared by the action of phenylcarbimide on mesitylhydroxylamine, crystallises from benzene in white, felted needles, and melts and decomposes at 116°.

iso*Benzaldoxime mesityl ether*, $\mathrm{C_6H_5\cdot CH}{<}\begin{smallmatrix}\mathrm{N\cdot C_6H_2Me_3}\\ |\\ \mathrm{O}\end{smallmatrix}$, prepared by the action of mesitylhydroxylamine on benzaldehyde, crystallises from light petroleum in transparent needles, melts at 101·5—102°, and is hydrolysed by dilute mineral acids. p-*Nitro*iso*benzaldoxime mesityl ether*,  $NO_2\cdot C_6H_4\cdot CH{<}\begin{matrix}N\cdot C_6H_2Me_3\\ |\\ O\end{matrix}$, forms yellow needles, and melts at 156·5—157°. m-*Nitro*iso*benzaldoxime mesityl ether* forms yellowish-white needles and melts at 140·5—141°. iso*Anisaldoxime mesityl ether*  $OMe\cdot C_6H_4\cdot CH{<}\begin{matrix}N\cdot C_6H_2Me_3\\ |\\ O\end{matrix}$, forms white, silky needles and melts at 152—152·5°.

Nitrosomesitylene, $C_6H_2Me_3\cdot NO$, crystallises in glistening, iridescent, orthorhombic tablets or needles and melts at 122° to a green liquid; at the freezing point of benzene, the solutions consist chiefly of double molecules, and are almost colourless, whilst at the boiling point the solutions are green, and the molecular weight is normal; the substance is decomposed by boiling water into nitromesitylene and mesidine, together with a small quantity of trimethyl-ψ-quinol; unlike nitrosobenzene, it does not reduce Fehling's solution, and does not condense with the hydroxylamine to form an azoxy-derivative.

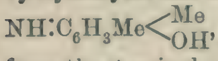
T. M. L.

Mesityl-ψ-quinol. By EUGEN BAMBERGER and ADOLF RISING (*Ber.*, 1901, 33, 3636—3642).—*Mesityl-ψ-quinol*, $O{:}C_6H_2Me_3\cdot OH$ (compare preceding page), prepared by passing a current of air through mesitylhydroxylamine suspended in water, crystallises from light petroleum in flat, white, glistening needles, and melts at 45·5—46°. The *benzoyl* derivative, $O{:}C_6H_2Me_3\cdot OBz$, forms glistening prisms and melts at 128·5°. By heating with sodium hydroxide in a current of hydrogen on a water-bath, the ψ-quinol is converted into cumoquinol,

$$C_6HMe_3(OH)_2\ [Me_3:(OH)_2=1:2:4:3:6];$$

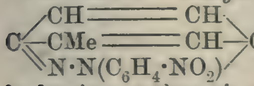
it is also readily reduced by zinc and ammonium chloride, sulphurous acid, or ferrous sulphate and sodium hydroxide to mesitol, $C_6H_2Me_3\cdot OH$.

T. M. L.

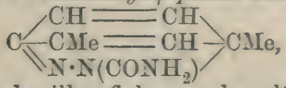
2 : 4-Dimethylphenylhydroxylamine and 2 : 4-Dimethyl-ψ-quinol. By EUGEN BAMBERGER and F. BRADY (*Ber.*, 1901, 33, 3642—3658).—as-*Azoxy*-m-*xylene*, $N_2O(C_6H_3Me_2)_2$, $[Me_2:N_2O=1:3:4]$, prepared by atmospheric oxidation of the hydroxylamine, forms glistening, yellow needles and melts at 76—76·5°. Dilute sulphuric acid at 100° converts the hydroxylamine into *as.m*-xylidine, nitroso-*m*-xylene, and azoxy-*m*-xylene, together with 2 : 4-dimethyl-ψ-quinol, and amino-*m*-xylenol, $[Me_2:OH:NH_2=1:4:2:5]$, which are probably produced by hydrolysis and reduction respectively from dimethylimino-ψ-quinol,  $NH{:}C_6H_3Me{<}\begin{matrix}Me\\ OH\end{matrix}$, and 2 : 4-dimethylquinol, formed by isomeric change from the ψ-quinol, which is the chief product of the action. Similar products are obtained at atmospheric temperatures, or by the action of alum solution, but the proportion of dimethyl-ψ-quinol is larger.

2 : 4-*Dimethyl-ψ-quinol hydrate*, $O{:}C_6H_3Me_2\cdot OH+H_2O$, crystallises in glistening, colourless, rhombic prisms, melts at 53—54° (corr.), and loses its water on exposure to the air. The *ψ-quinol* forms glistening, colourless prisms, melts at 73—73·5° (corr.), dissolves moderately in

boiling water and readily in most organic solvents, and volatilises at 100°. Sodium hydroxide at 100° converts it into the isomeric 2 : 4-dimethylquinol, no trace of 4 : 6-dimethylresorcinol being produced; acids act similarly, but give a much smaller yield of the quinol; the ψ-quinol is also decomposed by light; it is very readily reduced to *as.m*-xylenol. *Benzoyl-*2 : 4-*dimethyl-ψ-quinol*, $O{:}C_6H_3Me_2{\cdot}OBz$, crystallises from light petroleum in clear, glistening prisms and melts at 72·5—73·5°. *Anhydro-*2 : 4-*dimethyl-ψ-quinol-*p-*nitrophenylhydrazone*,



prepared by the action of *p*-nitrophenylhydrazine on the quinol, crystallises from alcohol in glistening, dark orange-red needles, melts at 126·5—127°, and is insoluble in alkali hydroxides. *Anhydro-*2 : 4-*dimethyl-ψ-quinol semicarbazone*,



separates in orange-red, silky flakes, and melts and decomposes at 134—135°. 2 : 4-*Dimethylimino-ψ-quinol*, $NH{:}C_6H_3Me_2{\cdot}OH$, has not been isolated in a pure state, but its presence is proved by continued decomposition into ammonia and the ψ-quinol. T. M. L.

Substance formed in the Iodination of Phenols. By Wilhelm Vaubel (*Chem. Zeit.*, 1900, **24**, 1059—1060; 1077—1078).—When a solution of phenol in saturated aqueous sodium hydrogen carbonate is treated at 25° with an excess of a solution of iodine in aqueous potassium iodide, an insoluble red substance is formed. This contains 64·7—64·8 per cent. of iodine, corresponding with 1⅓ I per mol. of phenol; when treated with alcoholic potash, it is converted into a white substance with 64·5 per cent. of iodine, and when reduced with zinc dust in alkaline alcoholic solution it forms a *compound*, $C_{18}H_{18}O_3$, which is a yellowish-brown powder soluble in alkalis, melts at 74—76°, and yields a *bromo*-derivative, $C_{18}H_{17}O_3Br$, when it is dissolved in acetic acid, and treated with aqueous potassium bromide, hydrochloric acid, and bromate.

Other phenols behave in a more or less similar manner when iodinated in sodium hydrogen carbonate solution, several molecules frequently condensing. The phenols are enumerated below, with the number of iodine atoms present in the product per mol. of the phenol. Salicylic acid, 1⅓ (with elimination of the carboxyl group); *m*-cresol, 2—3; *o*-cresol dibromide, 1; *o*-nitrophenol, 1·6; *p*-nitrophenol, 3; tyrosine, 0·5. Similar results by other observers are quoted in addition.

C. F. B.

Aryl Hydrogen Sulphates. By Albert Verley (*Bull. Soc. Chim.*, 1901, [iii], **25**, 46—49).—A general method for the preparation of potassium aryl sulphates consists in adding the phenol to a cooled mixture of pyridine and chlorosulphonic acid in carbon disulphide solution, removing the carbon disulphide by distillation, and decomposing the double sulphate of pyridine and the phenol thus produced by distillation with potassium hydroxide solution. *Potassium eugenyl sulphate* is thus obtained in the form of white, nacreous scales melting at 203°. When heated in acid solution it is decomposed, with the formation of eugenol and potassium hydrogen sulphate, whilst when boiled with excess of potash it is converted into potassium *iso*eugenyl sulphate which melts at 223°. This salt is readily converted into potassium vanillin sulphate by the action of oxidising agents, ozone being the most suitable. Potassium vanillin sulphate forms small, yellow crystals which decompose at 200°, and yields vanillin when heated with dilute sulphuric acid.

The method described has also been applied to the preparation of sodium phenyl sulphate, potassium phenyl sulphate, potassium thymyl sulphate melting at 80°, potassium β-naphthyl sulphate melting at 210°, potassium benzyl sulphate, which crystallises in brilliant, white needles melting at 233°, and potassium geranyl sulphate which does not crystallise. N. L.

Derivatives of Phenyl Ether. By A. N. Cook and Homer W. Hillyer (*Amer. Chem. J.*, 1900, **24**, 525—529).—*o-Nitrophenyl* p-*tolyl ether*, $NO_2\cdot C_6H_4\cdot O\cdot C_6H_4Me$, obtained by the action of *o*-bromonitrobenzene on the potassium derivative of *p*-cresol, crystallises in large, sulphur-yellow, monoclinic prisms, melts at 49°, boils at 220° under 25 mm. pressure, but suffers partial decomposition when distilled under the ordinary pressure; it is not volatile with steam; it dissolves easily in ether, acetic acid, chloroform, benzene, or hot alcohol.

2-*Nitro*-4′-*carboxyphenyl ether*, [4-o-*nitrophenoxybenzoic acid*],

$$NO_2\cdot C_6H_4\cdot O\cdot C_6H_4\cdot CO_2H,$$

prepared by oxidising *o*-nitrophenyl *p*-tolyl ether with a solution of chromium trioxide in glacial acetic acid, melts at 182—183°, crystallises from hot water in yellow needles, and is very soluble in glacial acetic acid or warm alcohol; its *cadmium*, *silver*, and *barium* salts are described.

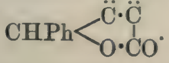
The *hydrochloride* of o-*aminophenyl*-p-*tolyl ether*,

$$NH_2\cdot C_6H_4\cdot O\cdot C_6H_4Me,HCl,$$

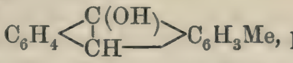
obtained by reducing the nitro-compound with tin and hydrochloric acid, crystallises in needles, and melts at 220°; the base may be precipitated from a solution of the hydrochloride, but rapidly decomposes; the *platinichloride* melts and decomposes at 150°. E. G.

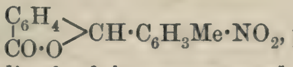
Derivatives of Cacodylic Acid. By A. Astruc and H. Murco (*J. Pharm.*, 1900, [vi], **12**, 553—556).—Guaiacol cacodylate (Barbary and Rebec, *Bull. Soc. Pharm.*, 1900, **11**, 121) crystallises in small prisms which are soluble in alcohol, glycerol, or water; it is a very unstable salt, and on solution in water is immediately decomposed into cacodylic acid and guaiacol, which separates out in oily drops.

Cinnamylcacodylic acid, $C_8H_7\cdot CO_2H,AsMe_2O\cdot OH$, prepared by the direct combination of mol. proportions of cacodylic acid and cinnamic acid, crystallises in prisms melting at 79—81°, and is only slightly soluble in ether, glycerol, or oils, but dissolves readily in alcohol. Cinnamic acid is precipitated on the addition of water to its alcoholic solutions. When treated with water it is decomposed into cacodylic acid, which dissolves in the water, and cinnamic acid, which remains undissolved. H. R. Le S.

Polymeric Phenyl*iso*crotonic Acid. By RUDOLPH FITTIG (*Ber.*, 1900, **33**, 3519—3521).—When phenyl*iso*crotonic acid is boiled for 6 hours with dilute hydrochloric acid (1 vol. commercial acid to 3 vols. of water), 65 per cent. of it is converted into phenylbutyrolactone; the reaction is never complete and the lactone when similarly boiled is partially converted into phenyl*iso*crotonic acid. When stronger acid is employed, the polymeric phenyl*iso*crotonic acid previously described (Abstr., 1888, 595) is also formed. It has the molecular formula, $C_{22}H_{20}O_4$, and is a monobasic lactonic acid and not dibasic; when oxidised, it yields benzoic acid and thus the group C_6H_5 must be intact. An intermediate product on oxidation is the *ketonic acid*, $C_{20}H_{20}O_5$, melting at 132°; when this is reduced, it is converted back into the lactonic acid; according to the author, this must contain the group,  $CHPh<\begin{matrix}\ddot{C}\cdot\ddot{C}\\ | \\ O\cdot CO\end{matrix}$. J. J. S.

***p*-Methyl-*o*-benzylbenzoic Acid.** By HEINRICH LIMPRICHT (*Annalen*, 1900, **314**, 237—251. Compare Abstr., 1898, i, 322).—*p*-Methyl-*o*-benzylbenzoic acid, $C_6H_4Me\cdot CH_2\cdot C_6H_4\cdot CO_2H$, crystallises from alcohol in large, six-sided plates, and melts at 133°; the *sodium* salt crystallises in long needles containing $2H_2O$, and melts at 270°, the *silver* salt is anhydrous, and the *methyl* ester crystallises from alcohol in thin, lustrous leaflets, and melts at 126°. The *chloride* is a yellow oil which does not combine with hydrocarbons under the influence of aluminium chloride, and when heated changes very readily into methylanthranol.

β-Methylanthranol,  $C_6H_4<\begin{matrix}C(OH)\\ | \\ CH\end{matrix}>C_6H_3Me$, prepared by the action of concentrated sulphuric acid on *p*-methyl-*o*-benzylbenzoic acid, is also produced when the acid chloride is heated at 95° in a vacuum; it crystallises from alcohol in plates, melts at 100°, and sublimes in needles and leaflets when strongly heated. Chromic acid oxidises the substance to β-methylanthraquinone. Solutions of methylanthranol in alkalis and alkali carbonates decompose rapidly, and besides methylanthraquinone, it has been found possible to isolate two *compounds* melting at 150° and 207° respectively; the latter has the composition $C_{30}H_{22}O_2$.

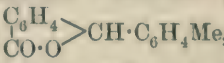
Nitrotolylphthalide,  $\begin{matrix}C_6H_4\\ | \\ CO\cdot O\end{matrix}>CH\cdot C_6H_3Me\cdot NO_2$, produced when methylbenzylbenzoic acid is dissolved in concentrated nitric acid, separates from alcohol in colourless crystals and melts at 137°. *Trinitromethylbenzylbenzoic acid*, $C_{15}H_{11}O_8N_3$, forms small, white crystals, and melts at 213°; the *barium* salt crystallises from water in colourless prisms. *Trinitrotoluoylbenzoic acid*, $C_{15}H_9O_9N_3$, crystallises from acetic acid in small prisms and melts at 215°; the *barium* salt contains $3H_2O$.

Aminomethylbenzylbenzoic acid, $NH_2\cdot C_6H_3Me\cdot CH_2\cdot C_6H_4\cdot CO_2H$, prepared by reducing nitrotolylphthalide and nitrotoluoylbenzoic acid with zinc dust and ammonia, crystallises from dilute alcohol in slender, white needles and melts at 155°; the *barium* and *silver* salts are anhydrous, and the *hydrochloride* and *nitrate* melt at 215° and 214° respectively. M. O. F.

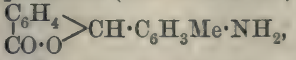
Dichlorohydroxybenzoic Acids. By N. Tarugi (*Gazzetta*, 1900, **30**, 487—492).—The action of chlorine on potassium salicylate yields a mixture of mono- and di-chlorosalicylic acids. In presence of increasing quantities of potassium hydroxide, the proportion of dichloro-acid formed increases, until the mixture consists of 3 mols. of potassium hydroxide to 1 mol. of salicylic acid, when the disubstituted acid alone is formed together with a small quantity of chlorophenol. If the proportion of potassium hydroxide be further increased, the dichloro-acid diminishes in quantity and finally vanishes, the amount of 2 : 4-dichlorophenol formed showing a corresponding increase. The dichlorosalicylic acid formed in the above reaction has the constitution [$CO_2H : OH : Cl_2 = 1 : 2 : 3 : 5$]; when heated with lime, it yields 2 : 4-dichlorophenol, whilst with nitric acid the dichloronitrophenol [$OH : Cl_2 : NO_2 = 1 : 2 : 4 : 6$] is obtained. Similarly, the action of excess of chlorine on a solution of 1 mol. of *p*-hydroxybenzoic acid in 3 mols. of potassium hydroxide solution yields the dichlorohydroxybenzoic acid of the constitution [$CO_2H : Cl : OH : Cl = 1 : 3 : 4 : 5$]; this acid with nitric acid gives 2 : 6-dichloro-4-nitrophenol, whilst when heated with lime it yields 2 : 6-dichlorophenol, which is also obtained in increasing quantities as the proportion of potassium hydroxide in the above reaction is increased beyond 3 mols. The action of chlorine on *o*-nitrophenol (1 mol.) dissolved in potassium hydroxide (3 mols.) solution yields 2 : 4-dichloro-6-nitrophenol, whilst when *p*-nitrophenol is employed, 2 : 6-dichloro-4-nitrophenol is obtained.

Thus when an excess of chlorine acts in alkaline solution on a disubstituted benzene derivative having an acid function, two atoms of chlorine enter the benzene nucleus and, in the case of *o*- or *p*-compounds, always take up given stable positions. T. H. P.

Tautomerism of *o*-Benzoylbenzoic Acid. By Albin Haller and Alfred Guyot (*Bull. Soc. Chim.*, 1901, [iii], **25**, 49—56).—The unsuccessful attempts to prepare two methyl esters corresponding with the two hypothetical tautomeric forms of benzoylbenzoic acid have already been described (Abstr., 1900, i, 170). It is now also shown that the acid behaves normally when heated with phenylcarbimide at 80°, diphenylcarbamide and benzoylbenzoic anhydride being formed. At the ordinary temperature, however, an unstable additive product seems to be produced. N. L.

Tolylphthalide. By Heinrich Limpricht (*Annalen*, 1900, **314**, 251—258).—Tolylphthalide,  $\left.\begin{matrix}C_6H_4\\ | \\ CO{\cdot}O\end{matrix}\right>CH{\cdot}C_6H_4Me$, crystallises in long, flat, colourless needles melting at 129°, and distils under 15 mm. pressure without decomposing; it dissolves in alkalis and alkali carbonates, but the acid, of which salts are thereby produced, cannot be isolated. Ammonia and zinc dust convert it into methylbenzylbenzoic acid, and potassium permanganate oxidises it to toluoylbenzoic and benzophenonedicarboxylic acids.

Concentrated nitric acid converts the substance into nitrotolylphthalide (this vol., i, 145) which melts at 137°. *Aminotolylphthalide*,



$\begin{array}{l}C_6H_4\\ \vert \\ CO\cdot O\end{array}\!\!>CH\cdot C_6H_3Me\cdot NH_2$, obtained by reducing the nitro-derivative with stannous chloride, crystallises in colourless, four-sided, rhombic plates melting at 144°; the *nitrate* and *hydrochloride* crystallise in slender, long needles, and the latter decomposes at 205°. *Trinitrotolylphthalide*, $C_{15}H_9O_8N_3$, crystallises from acetone in white, microscopic leaflets, and melts at 215°.

M. O. F.

Isomeric Ammonia Derivatives of Ethyl Benzylidenebisacetoacetate. (Benzylideneacetoacetic-β-aminocrotonate or Phenylaminohepteneonedicarboxylate.) By PAUL RABE (*Ber.*, 1900, **33**, 3803—3806).—Ethyl β-benzylidenebisacetoacetate is readily converted by ammonia into *ethyl δ-phenyl-β-amino-β-heptene-ζ-one-γ : ε-dicarboxylate*, $NH_2\cdot CMe\vdots C(CO_2Et)\cdot CHPh\cdot CHAc\cdot CO_2Et$, which exists in two distinct forms. The α-form consists of woolly needles, which melt at 58° and then pass into the β-form. The β-form separates from alcoholic solution in coarse, well-developed crystals melting at 98°. When water is added to an alcoholic solution of either form, a *hydrate* is produced which contains $1H_2O$, melts at about 72°, and over sulphuric acid loses water and yields the α-form. The two forms are alike in their behaviour towards alcoholic ferric chloride, and the exact nature of their isomerism has not yet been ascertained.

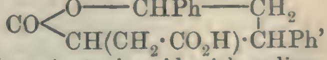
A. H.

Addition of Diethyl Succinate to αβ-Unsaturated Ketones and Esters. By HANS STOBBE (*Annalen*, 1900, **314**, 111—146. Compare Abstr., 1899, i, 900; 1900, i, 179).—[With KARL RUSSWURM].—*γ-Phenacyl-γ-phenylpyrotartaric acid*,

$$COPh\cdot CH_2\cdot CHPh\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H,$$

produced in the form of its sodium derivative when an ethereal solution of benzylideneacetophenone and diethyl succinate is added to sodium ethoxide suspended in ice-cold ether, crystallises from water or ether in rhombic plates, and melts at 175—177°; it is sparingly soluble in cold water, and requires 500 parts of hot benzene for dissolution. The *sodium* salt forms long needles containing $4\frac{1}{2}H_2O$, the *barium* salt contains $3H_2O$, and the *calcium* and *silver* salts are amorphous. The *dimethyl* ester crystallises from a mixture of ether and light petroleum in large plates melting at 77—79°, and the *diethyl* ester melts at 60—62°; the *anhydride* crystallises from a mixture of benzene and light petroleum in stellate aggregates of needles, and melts at 119—121·5°. The *oxime* is sparingly soluble in water, from which it separates in minute crystals, melting at 180—184°, when it becomes deep red; the *semicarbazone* melts and evolves gas at 194—198°, and forms a crystalline *sodium* derivative, which becomes yellow at 200°, and decomposes completely at 245—250°.

βδ-Diphenylvalerolactoneacetic acid,

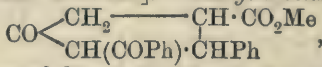


$CO\!<\!\begin{array}{l}O\text{——}CHPh\text{——}CH_2\\ \qquad\qquad\qquad\qquad\quad \vert \\ CH(CH_2\cdot CO_2H)\cdot CHPh\end{array}$,

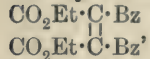
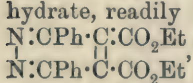
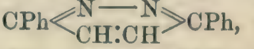
prepared by reducing γ-phenacyl-γ-phenylpyrotartaric acid with sodium amalgam, crystallises from 50 per cent. alcohol in lustrous needles, which soften at 170°, and melt between 185° and 187°. The *barium* salt of the hydroxydicarboxylic acid, $C_{19}H_{20}O_3$, obtained by heating the lactone-acid with barium hydroxide, crystallises in leaflets.

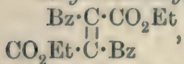
When phenacylphenylpyrotartaric acid is oxidised with nitric acid, it is decomposed completely, yielding only benzoic acid and its products of nitration. Potassium permanganate, however, gives rise to β-benzoylpropionic and benzoylformic acids.

The *compound*, $C_{29}H_{26}O_4$, a bye-product in the preparation of γ-phenacyl-γ-phenylpyrotartaric acid, crystallises from 90 per cent. alcohol in slender needles, and melts at 224—227°.

[With RICHARD FISCHER].—*Methyl 2-benzoyl-3-phenyl*cyclo*pentanone-4-carboxylate*,  $CO<\begin{array}{l}CH_2\text{———}CH\cdot CO_2Me\\ CH(COPh)\cdot CHPh\end{array}$, prepared by adding an ethereal solution of dimethyl-γ-phenacyl-γ-phenylpyrotartrate to sodium methoxide suspended in ether, and acidifying the product, crystallises from absolute alcohol in slender needles and melts at 115—116°; the *semicarbazone* melts and decomposes at 231—232°. M. O. F.

Dibenzoylmaleic and Dibenzoylfumaric Esters. By CARL PAAL and HEINRICH SCHULZE (*Ber.*, 1900, 33, 3784—3795).—Ethyl dibenzoylethylenedicarboxylate exists in *cis*- and *trans*-forms, the configurations of which have been determined by their reaction with hydrazine hydrate. This substance reacts with the *cis*-form almost quantitatively to produce a pyridazine derivative, whilst with the *trans*-form it only reacts slowly and incompletely to produce the same compound.

Ethyl dibenzoylmaleate (ethyl *cis*-dibenzoylethylenedicarboxylate),  $\begin{array}{l}CO_2Et\cdot C\cdot Bz\\ CO_2Et\cdot C\cdot Bz\end{array}$, which was formerly described by Paal and Härtel (Abstr., 1897, i, 598) as ethyl dibenzoylfumarate, when treated with hydrazine hydrate, readily yields *ethyl 3 : 6-diphenylpyridazine-4 : 5-dicarboxylate*,  $\begin{array}{l}N{:}CPh\cdot C{:}CO_2Et\\ N{:}CPh\cdot C\cdot CO_2Et\end{array}$, which crystallises in long, flat, colourless needles melting at 127—128° *Diphenylpyridazinedicarboxylic acid* crystallises in long needles containing 2 mols. of alcohol, and melts and decomposes at 202°. The *potassium* salt crystallises in silky needles, and the *silver* salt in sparingly soluble, microscopic needles. When the acid is heated above its melting point, it yields carbon dioxide and *3 : 6-diphenylpyridazine*,  $CPh<\begin{array}{c}N\text{——}N\\ CH{:}CH\end{array}>CPh$, which crystallises in large, nacreous plates melting at 221—222°. The crystalline *hydrochloride*, *aurichloride*, and *platinichloride* are all decomposed by water.

Ethyl dibenzoylfumarate (ethyl *trans*-dibenzoylethylenedicarboxylate),  $\begin{array}{l}\;\;Bz\cdot C\cdot CO_2Et\\ CO_2Et\cdot C\cdot Bz\end{array}$, is formed when the *cis*-compound is heated with a small amount of aniline in a closed vessel at 100°, and crystallises in well developed, colourless, asymmetric prisms melting at 87—88°. Both ethyl dibenzoylmaleate and ethyl dibenzoylfumarate are reduced by phenylmethylhydrazine to ethyl dibenzoylsuccinate. When the fumaric ester is treated with alcoholic potash at the ordinary temperature, pure potassium dibenzoylfumarate is formed, which crystallises in flat needles containing alcohol. The *silver* salt, which is a faintly yellow, microcrystalline powder, is converted by ethyl iodide almost quantitatively into the original ethyl dibenzoylfumarate. When a solution of the potassium salt is acidified, the acid obtained is not dibenzoylfumaric acid, but dibenzoylmalic acid, $CO_2H\cdot CBz(OH)\cdot CHBz\cdot CO_2H$ (Paal and Härtel). On the other hand, this acid does not yield corresponding salts, but when treated with the requisite amount of aqueous potash yields potassium dibenzoylfumarate. That the acid is not dibenzoylfumaric acid containing $1H_2O$ is proved by the fact that by heating the water cannot be removed without decomposition occurring (compare this vol., i, 154).

Ethyl dibenzoylmaleate is converted by hydrolysis into a mixture of potassium dibenzoylmaleate with a small amount of potassium dibenzoylfumarate. This mixture of potassium salts is decomposed by acids in a similar manner to potassium dibenzoylfumarate, dibenzoylmalic acid being produced. A. H.

Lichens and their Characteristic Constituents. V. By OSWALD HESSE (*J. pr. Chem.*, 1900, [ii], **62**, 430—480. Compare Abstr., 1898, i, 531, 679; 1899, i, 381; this vol., i, 85).—*Usnea plicata* from Java cinchona bark contains *d*-usnic acid, usnaric acid, usnarin and plicatic acid. Usnaric acid contains no alkyloxy-groups; when heated with alcoholic potassium hydroxide or aqueous barium hydroxide, it loses carbon dioxide, and a brown, amorphous substance is produced. If a solution of usnaric acid in acetic anhydride is heated for 24 hours and allowed to cool, a *substance*, which melts at 209° and is slightly soluble in alcohol, separates in white needles; on diluting the mother-liquor with water, another substance is obtained, which melts at 128°, and dissolves readily in alcohol; both these compounds exhibit an acid reaction, and do not give any coloration with ferric chloride. *Plicatic acid*, $C_{20}H_{33}O_8\cdot OMe$, is dibasic; it crystallises in lustrous, white leaflets, melts at 133°, dissolves easily in alcohol, acetone, or ether, and gives no coloration with ferric chloride; its *barium* salt was prepared.

Usnea barbata var. *dasypoga* and *florida* yield *d*-usnic acid, usnaric acid and alectoric acid (see later).

Alectoria jubata var. *implexa* (*Bryopogon jubatum* var. *implexum*) contains not only salazinic acid as stated by Zopf (Abstr., 1898, i, 90), but also alectoric acid. *Alectoric acid* is dibasic; it dissolves sparingly in alcohol, ether, or hot glacial acetic acid, and crystallises from the last-mentioned solvent in needles; it melts and decomposes at 186°, gives a reddish-brown coloration with ferric chloride, contains no alkyloxy-groups, and is converted by acetic anhydride into a colourless resin; its *barium* and *potassium* salts are described. When this acid is heated with solution of barium hydroxide, the solution becomes dark red, and yields an *acid*, which crystallises in white needles, is more soluble in ether or alcohol than alectoric acid, and melts and decomposes at about 220°.

Evernia divaricata does not contain usnic acid as asserted by Zopf (Abstr., 1898, i, 90), but only divaricatic acid.

Ramalina cuspidata yields *cuspidatic acid*, $C_{16}H_{20}O_{10}$, which crystallises in white needles, melts at 218°, dissolves easily in ether, acetone, or alcohol, and gives a violet-blue coloration with ferric chloride.

Thamnolic acid, $C_{19}H_{15}O_{10}\cdot OMe$, obtained from *Thamnolia vermicularis* (Abstr., 1899, i, 381), melts and decomposes at 213°; when this acid is heated with barium hydroxide solution, it loses carbon dioxide and yields *thamnolinic acid*, $C_{16}H_{20}O_7$, which crystallises in long, colourless needles, melts at 163°, dissolves readily in alcohol, ether, glacial acetic acid, or hot water, and gives a purple coloration with ferric chloride.

Stereocaulon coralloides contains atranorin, a small quantity of usnetic acid, and an *acid*, which Zopf (Abstr., 1896, i, 103) seems to have mistaken for psoromic acid (parellic acid); this new acid crystallises in small, white needles, is soluble in hot glacial acetic acid, hot alcohol, hot acetone, or benzene, and gives a violet-blue coloration with ferric chloride; when heated, it does not melt, but darkens at 250° and is quite black at 260°.

The 'stereocaulic acid' obtained by Zopf from *S. alpinum* is identical with usnetic acid.

S. salazinum contains not only salazinic acid, as stated by Zopf (Abstr., 1897, i, 362), but also a considerable quantity of atranorin. Salazinic acid contains no alkyloxy-groups; it crystallises from hot alcohol in spherical, crystalline aggregates, and blackens at 260—262° without melting. It dissolves in dilute potassium hydroxide to form a yellow solution which rapidly darkens, and yields red crystals of the potassium salt of an *acid*, which is a decomposition product of salazinic acid; the same acid is produced when salazinic acid is dissolved in concentrated sulphuric acid.

Cladonia Floerkeana yields coccellic acid, as previously shown by the author (Abstr., 1899, 382), and also a small proportion of thamnolic acid. When coccellic acid is heated with hydriodic acid, it is converted into a mixture of rhizonic and coccellinic acids, the former of which suffers decomposition with formation of methyl iodide, carbon dioxide, and betorcinol, whilst the latter remains unchanged. *Coccellinic acid*, $C_{10}H_{12}O_4$, crystallises in white needles, melts at 176—177°, dissolves easily in ether or alcohol, and gives an intense violet-blue coloration with ferric chloride; if heated above its melting point, it decomposes and yields a crystalline sublimate, which is probably mesorcinol.

C. fimbriata (*ε-chordalis*) yields protocetraric acid.

C. uncinata does not contain usnic acid, as stated by Knop (*Annalen*, 1844, 49, 124), but *uncinatic acid*, $C_{23}H_{28}O_9$, is obtained as a white, crystalline powder which melts and decomposes at 212°, is sparingly soluble in ether, chloroform, glacial acetic acid, or cold alcohol, but freely in hot alcohol, and gives a purple coloration with ferric chloride; its *potassium*, *ammonium*, and *barium* salts were prepared.

C. squamosa (*α-ventricosa*) yields *squamatic acid*, which crystallises in short prisms, melts and decomposes at 215°, has a slightly bitter taste, dissolves sparingly in ether, alcohol, benzene, chloroform, or acetone, and more easily in glacial acetic acid, and gives a purple coloration with ferric chloride; it contains one methoxyl group.

Parmelia tiliacea (*Imbricaria tiliacea*).—Re-examination of this lichen has confirmed the opinion previously expressed by the author (Abstr., 1899, i, 382) that Zopf's 'parmelialic acid' is identical with lecanoric acid.

P. sorediata contains lecanoric acid but no atranorin.

P. perlata.—The lichen previously examined by the author consisted of a mixture of *P. perlata*, *P. perforata*, and *P. olivetorum*.

P. perlata yields atranorin and a trace of lecanoric acid.

P. perforata furnished atranorin and a small proportion of lecanoric acid, whereas Zopf (Abstr., 1898, i, 90) found salazinic acid and very little atranorin.

P. olivetorum proved on re-examination to contain atranorin and lecanoric acid, as previously stated (Abstr., 1898, i, 679), but not erythric acid, as Zopf asserts.

P. tinctorum (= *P. coralloides*) yields atranorin and 23·58 per cent. of lecanoric acid.

P. saxatilis var. *sulcata* furnished protocetraric acid only, whereas Zopf (Abstr., 1897, i, 436) found atranorin and 'stereocaulic acid.'

P. saxatilis var. *panniformis* contains atranorin, protocetraric acid, and usnetic acid (Abstr., 1877, ii, 896). Usnetic acid has the composition $C_{24}H_{26}O_8$, and not $C_9H_{10}O_3$ as previously stated; it melts at 192°. When usnetic acid is heated with barium hydroxide, it yields carbon dioxide and *usnetol*, $C_{23}H_{28}O_7$, which crystallises in white needles, melts at 166°, and is very soluble in ether or alcohol; a small quantity of another *substance* is also produced, which crystallises in white needles, and is soluble in ether, but differs from usnetol in being insoluble in solution of potassium hydrogen carbonate.

P. acetabulum contains atranorin and salazinic acid, as previously shown by Zopf (Abstr., 1898, i, 489).

Umbilicaria pustulata yields gyrophoric acid, which melts at 200—202°, dissolves easily in alcohol or acetone, is optically inactive, and contains no alkyloxy-groups. The formula $C_{18}H_{20}O_7$ was previously assigned to this acid, but the author now finds that it is isomeric with lecanoric acid, $C_{16}H_{14}O_7$. When gyrophoric acid is heated with glacial acetic acid, it is converted into orsellic acid; if boiled with alcohol, it yields orsellic acid and ethyl orsellate; under other conditions, the acid decomposes into orcinol and carbon dioxide. The author considers that gyrophoric and lecanoric acids are probably the *cis-* and *trans*-forms of the acid,

$$CO_2H\cdot C_6H_2Me(OH)\cdot O\cdot CO\cdot C_6H_2Me(OH)_2.$$

Placodium saxicolum var. *compactum* furnishes atranorin, and a crystalline *acid*, which is soluble in alcohol or ether.

P. gypsaceum yields parellic acid, but no usnic acid, as stated by Zopf (Abstr., 1898, i, 90).

P. circinatum contains parellic acid.

Icmadophila æruginosa furnished only an uncrystallisable brown oil, whereas Bachmann obtained icmadophilic acid.

Blastenia arenaria var. *teicholytum* (*Callopisma teicholytum*).—Re-examination of this lichen has confirmed the author's view (Abstr., 1899, i, 382) that it contains atranorin and gyrophoric acid.

Hæmatomma ventosum contains *d*-usnic acid, divaricatic acid, and an *acid* which does not possess the properties of the ventosaric acid described by Zopf (Abstr., 1897, i, 364), but rather resembles alectoric acid.

Lecanora subfusca yields atranorin, as found by Zopf (Abstr., 1897, i, 436).

Aspicilia calcarea furnishes *aspicilin*, which crystallises in white prisms, melts at 178·5°, dissolves readily in hot alcohol, glacial acetic acid, chloroform, or benzene, but less easily in ether; when heated strongly, it sublimes and distils without decomposition. This lichen also contains oxalic acid and erythric acid (Abstr., 1898, i, 532), which the author now considers to be either erythrolecanoric or erythrogyrophoric acid.

Urceolaria scruposa var. *arenaria* yields a small proportion of lecanoric acid.

Lecidea grisella furnishes gyrophoric acid.

Graphis scripta yields salazinic acid.

An appendix to the paper contains a detailed criticism of Zopf's recent work (this vol., i, 87). E. G.

Usnic Acid. Rotation of other Lichen Acids. By HEINRICH SALKOWSKI (*Annalen*, 1900, **314**, 97—111. Compare Widman, Abstr., 1900, i, 235).—The author has examined specimens of usnic acid derived from more than twenty different lichens, and finds that although considerable variations in the melting point occur, the limits of specific rotatory power are comparatively narrow.

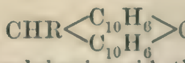
Analyses of the insoluble yellow barium, strontium, and calcium salts of usnic acid are given.

Rhizocarpic acid is optically active, but atranoric, chrysophanic, pinastric, soloric, usnolic, and vulpic acids, and calicyn, are inactive.

M. O. F.

Action of β-Naphthol on Aldehydes. By M. ROGOFF (*Ber.*, 1901, **33**, 3535—3538).—In continuation of Claisen's work (Abstr., 1887, 494) the author has prepared the following compounds by heating β-naphthol with aldehydes and acetic acid in closed tubes at 190—200°.

$C_{28}H_{20}O_3$, from vanillin, separates from glacial acetic acid in microscopic needles melting at 211°. $C_{28}H_{18}O_3$, from piperonaldehyde, crystallises in six-sided tablets melting at 237°. $C_{30}H_{24}O$, from cuminaldehyde, forms microscopic tablets and melts at 238°. $C_{28}H_{20}O_2$, from anisaldehyde, forms six-sided plates melting at 208°. $C_{27}H_{18}O_2$, from salicylaldehyde, crystallises in long prisms and melts at 208°.



These compounds are all of the type $CHR{<}{\substack{C_{10}H_6\\C_{10}H_6}}{>}O$, and are insoluble in alkalis; when warmed with sulphuric acid, they assume varying tints of red, and at the same time exhibit a greenish fluorescence. A. L.

Intramolecular Rearrangement of *iso*Aldoxime Ethers. By FRIEDRICH WEGENER (*Annalen*, 1900, **314**, 231—236. Compare Neubauer, Abstr., 1898, i, 134).—Contrary to a previous conclusion, the transformation of benzyl-*m*-nitro*iso*benzaldoxime into *m*-nitrobenzyl*iso*benzaldoxime is reversible. The same remark applies to the relation between *o*-chlorobenzyl*iso*benzaldoxime and benzyl-*o*-chloro*iso*benzaldoxime. M. O. F.

Benzophenone-*o*-sulphonic Acid and some of its Homologues.

By Carl Krannich (*Ber.*, 1900, **33**, 3485—3494).—Details are given for preparing ammonium *o*-sulphobenzoate from its imide ("saccharin"); it forms orthorhombic crystals [$a:b:c = 0{\cdot}6686:1:1{\cdot}2103$]. *o*-Sulphobenzoic acid crystallises with $3H_2O$ and melts at 69°, the anhydrous acid melting at 134°.

The following compounds were prepared by heating *o*-sulphobenzoic anhydride in presence of acetyl chloride with benzene and its homologues.

Benzophenonesulphonic [*benzoylbenzenesulphonic*] *acid*,

$$COPh{\cdot}C_6H_4{\cdot}SO_3H,$$

is very soluble in water, and cannot be obtained crystalline. The *ammonium* salt, with $1H_2O$, forms monoclinic crystals [$a:b:c = 1{\cdot}9224:1:1{\cdot}5921$; $\beta = 108°20'$] and melts at 202°; the potassium salt (Remsen and Saunders, Abstr., 1895, i, 474), with $1H_2O$, melts at 211°; the *sodium* salt, with $4H_2O$, melts at 60°, the anhydrous salt melting at 236°; the *barium* salt, with $1H_2O$, melts at 197—198°.

p-*Methylbenzoylbenzene*-o-*sulphonic acid*, $C_6H_4Me{\cdot}CO{\cdot}C_6H_4{\cdot}SO_3H$, prepared from toluene, is very deliquescent; the *ammonium* salt, with $1H_2O$, melts at 104°; the *potassium* salt, with $1H_2O$, melts at 248°; the *sodium* salt, with $4H_2O$, melts initially at 53°, and, when anhydrous, at 247°; the *barium* salt, with $1H_2O$, melts at 215°. The structure of the acid follows from its yielding *p*-toluic acid when fused with alkali.

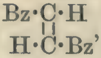
The substance obtained by the interaction of *m*-xylene and *o*-sulphobenzoic anhydride in presence of aluminium chloride is, by analogy with similar reactions (Abstr., 1882, 848, and 1896, i, 462), probably 2 : 4-*dimethylbenzoylbenzene*-o-*sulphonic acid*, $C_6H_3Me_2{\cdot}CO{\cdot}C_6H_4{\cdot}SO_3H$; it crystallises in slender, white needles with $2H_2O$, melts at 80°, and yields an *ammonium* salt, with $\frac{1}{2}H_2O$, melting at 235—236°. The *potassium* salt (anhydrous) melts and darkens at 300°; the *sodium* salt could not be obtained crystalline; the *barium* salt, with $2H_2O$, melts at 207°.

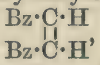
The ψ-cumene derivative is probably a 2 : 4 : 5-*trimethylbenzoylbenzene*-o-*sulphonic acid*, $C_6H_2Me_3{\cdot}CO{\cdot}C_6H_4{\cdot}SO_3H$ (compare Abstr., 1887, 940); it crystallises from chloroform in slender, white needles, sinters at 167°, melts at 169°, and yields an easily soluble, crystalline *ammonium* salt melting at 255—256°; the *potassium* salt melts and decomposes at 286°; the *sodium* salt, with $1\frac{1}{2}H_2O$, sinters at 272° and melts at 274°; the *barium* salt melts at 267°.

s-*Trimethylbenzoylbenzene*-o-*sulphonic acid*, obtained by using mesitylene, crystallises from water, in which it is sparingly soluble, in colourless, lustrous plates, with $4H_2O$, which melt at 98°, lose their contained water at 100—110°, and then melt at 184°; the *ammonium* salt melts at 272°, the *potassium* salt begins to sinter at 315°, the *sodium* salt, with $1H_2O$, melts at 171°, whilst the *barium* salt, with $4H_2O$, sinters at 248° and melts at 252°. W. A. D.

Action of Nitrogen Tetroxide on the Benzilmonoximes. By Giacomo Ponzio (*J. pr. Chem.*, 1900, [ii], 62, 543—544).—When an ethereal solution of α- or γ-benzilmonoxime is treated with nitrogen tetroxide, benzil, *p*-nitrobenzil, and small quantities of benzoic and *p*-nitrobenzoic acids are produced, but neither phenyldinitromethane nor its benzoyl derivative is formed. E. G.

The Stereoisomeric Symmetrical Dibenzoylethylenes. By Carl Paal and Heinrich Schulze (*Ber.*, 1900, 33, 3795—3800. (Compare this vol., i, 148).—When dibenzoylmalic acid is heated above its melting point, it loses water and carbon dioxide, and is converted into a mixture of the two stereoisomeric dibenzoylethylenes.

trans-*Dibenzoylethylene*,  $\begin{array}{c}Bz\cdot C\cdot H\\ \| \\ H\cdot C\cdot Bz\end{array}$, is the chief product of this decomposition, and crystallises in long, deep yellow needles melting at 111°. By reduction, it is converted into diphenacyl and combines with bromine to form *dibenzoylethylene bromide*, $COPh\cdot CHBr\cdot CHBr\cdot COPh$, which crystallises in small, white prisms melting at 178°. When warmed with hydrazine hydrate, it yields about 25 per cent. of the calculated amount of 3 : 6-diphenylpyridazine. It also combines with aniline to form *anilinodibenzoylethane* (anilinodiphenacyl), $NHPh\cdot CHBz\cdot CH_2Bz$, which crystallises in thin, sulphur-yellow prisms melting at 138° and is decomposed by boiling with acetic acid into the original *trans*-dibenzoylethylene and aniline.

cis-*Dibenzoylethylene*,  $\begin{array}{c}Bz\cdot C\cdot H\\ \| \\ Bz\cdot C\cdot H\end{array}$, which is only formed in small amount by the decomposition of dibenzoylmalic acid, crystallises in colourless, silky needles melting at 134°, and is more readily soluble in most reagents than the *trans*-modification. By hydrazine hydrate in the cold, it is converted quantitatively into 3 : 6-diphenylpyridazine and hence must have the *cis*-configuration. It unites with aniline to form the same anilinodiphenacyl as the *trans*-form, and also forms a *dibromide*. A. H.

Thermochemistry of Quinones: Constitution of Quinhydrones. By Amand Valeur (*Ann. Chim. Phys.*, 1900, [vii], 21, 470—574).—The thermochemical data relating to the unsubstituted quinones and their dihydro-derivatives have already been published (Abstr., 1898, ii, 420, 500). The following constants have been determined for the chlorine derivatives of quinone (see table, p. 155).

The heats of oxidation of the monochloro-, dichloro-, trichloro-, and tetrachloro-quinols to the corresponding quinones are 29·4, 35·6, 46·7, and 45·3 Cal. respectively.

The substitution of two chlorine atoms by two hydroxyl groups in the formation of chloroanilic acid from chloroanil is accompanied by a generation of 92 Cal.; this value approximates to the heat change which attends the production of a dibasic acid from its dichloride, the heat of hydrolysis of malonic chloride being 103·7 Cal.

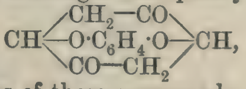
Sodium chloroanilate is described as a red compound crystallising with $4H_2O$; the author has obtained another hydrate containing $3H_2O$ which forms opaque, black crystals; the latter separates from concen-

	Heat of combustion.		Heat of formation from elements.	Heat of substitution of chlorine for hydrogen.
	Constant volume.	Constant pressure.		
Chloroquinone	618·5 Cal.	618·2 Cal.	56·0 Cal.	32·6 Cal.
Chloroquinol	647·6	647·6	95·6	30·6
2 : 6-Dichloroquinone	580·9	580·4	64·2	62·8
2 : 6-Dichloroquinol	615·9	615·7	97·9	54·6
Trichloroquinone	548·6	547·8	67·2	87·8
Trichloroquinol	595·0	594·5	89·5	68·2
Tetrachloroquinone	520·1	519·0	66·4	109·0
Tetrachloroquinol	566·1	564·3	90·1	90·8
Chloroanilic acid	487·3	486·2	158·4	

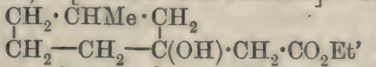
trated solutions at 35°, whilst the former is produced at 18°. The paper contains a detailed account of the estimation of halogens in organic compounds by the calorimetric bomb, and a description of a method for the quantitative estimation of quinones (compare Abstr., 1900, ii, 57 and 172). The action of hydroxylamine on the quinones under varying conditions has been studied; it is found to reduce the *p*-quinones with considerable generation of heat, and in this way, tetrachloroquinol is readily obtained from chloroanil.

The thermochemical data deduced from the study of the quinonemonoximes have already been published (Abstr., 1898, ii, 500).

A quinhydrone is produced by the direct combination of a quinone of higher molecular weight with the dihydro-derivative of a quinone of lower molecular weight, and the same product is obtained by mixing the less complex quinone with the quinol of higher molecular weight. In the second mode of formation, the first action is probably the oxidation of the quinol by the quinone of lower molecular weight, owing to the fact that the heat of reduction of the simpler quinone is greater than that of the quinone of higher molecular weight.

This hypothesis is justified by the fact that quinone and dihydroxyphenanthrene interact, forming quinol and phenanthraquinone. The author discusses the formulæ suggested by Graebe and by Jackson and Oenslager for quinhydrones and suggests the following constitution,  $\mathrm{CH}\left\langle\begin{matrix}\mathrm{CH_2{-}CO}\\ \mathrm{{-}O{\cdot}C_6H_4{\cdot}O{-}}\\ \mathrm{CO{-}CH_2}\end{matrix}\right\rangle\mathrm{CH}$, as being most in accordance with the properties of these compounds.

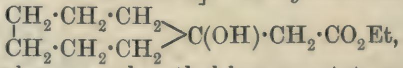
G. T. M.

Terpenes and Ethereal Oils. By Otto Wallach (*Annalen*, 1900, 314, 147—167).—[With Julius Salkind].—*Ethyl β-methyl*cyclo*hexanolacetic acid*,  $\begin{matrix}\mathrm{CH_2\cdot CHMe\cdot CH_2}\\ |\qquad\qquad\qquad |\\ \mathrm{CH_2{-}CH_2{-}C(OH)\cdot CH_2\cdot CO_2Et}\end{matrix}$, produced by the action of zinc on a mixture of methylhexanone and ethyl bromoacetate, is a liquid having the odour of ethyl benzoate; it boils at 127—129° and 254—256° under pressures of 21 mm. and 760 mm.

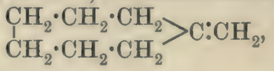
respectively, has a sp. gr. 1·0035, and n_D 1·4581 at 18°. The *methyl* ester boils at 120—125° and 240° under pressures of 23 mm. and 760 mm. respectively.

*Ethyl β-methyl*cyclo*hexeneacetate*, $C_7H_{11}\cdot CH_2\cdot CO_2Et$, obtained on heating ethyl methylhexanolacetate with finely powdered potassium hydrogen sulphate at 160° during 2—3 hours, boils at 111—112° and 229—231° under pressures of 23 mm. and 760 mm. respectively, has a sp. gr. 0·9555, and n_D 1·46207 at 20°. The *methyl* ester boils at 103—105° and 214—217° under pressures of 23 mm. and 760 mm. respectively; it has a sp. gr. 0·97 and n_D 1·4635 at 25°. *β-Methyl*cyclo*hexeneacetic acid*, $C_7H_{11}\cdot CH_2\cdot CO_2H$, boils at 146—149° and 245—255° under pressures of 23 mm. and 760 mm. respectively; it has a sp. gr. 1·015 and n_D 1·4807 at 27°. The *amide* crystallises from dilute methyl alcohol in colourless leaflets and melts at 149—150°.

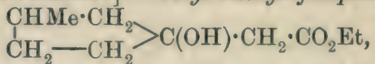
[With VAN BEECK-VOLLENHOVEN].—*Methylsuberolacetate*,



$$\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\cdot CH_2\end{matrix}\!>C(OH)\cdot CH_2\cdot CO_2Et,$$

prepared from suberone and methyl bromoacetate under the influence of zinc, boils at 141—145° and 249—257° under pressures of 12 mm. and 760 mm. respectively; it has a sp. gr. 1·037 and n_D 1·47017 at 20°. *Methyl subereneacetate*, $C_8H_{13}\cdot CO_2Me$, obtained from the foregoing substance and potassium hydrogen sulphate, boils at 125—126° under 13 mm. pressure; the *ethyl* ester boils at 135—136° under 23 mm. pressure. *Subereneacetic acid*, $C_9H_{14}O_2$, is a viscous liquid which boils at 158—159° under 17 mm. pressure, has a sp. gr. 1·035 and n_D 1·4920 at 20°. The *hydrocarbon*, C_8H_{14}, produced when subereneacetic acid is distilled under atmospheric pressure, boils at 138—140°, has a sp. gr. 0·824, and n_D 1·4611 at 20°; its constitution is probably represented by the expression  $\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\cdot CH_2\end{matrix}\!>C\colon CH_2$, the formula of a methylene*cyclo*heptane.

[With NICOLAI SPERANSKI].—*Ethyl methyl*cyclo*pentanolacetate*,



$$\begin{matrix}CHMe\cdot CH_2\\ |\\ CH_2\text{—}CH_2\end{matrix}\!>C(OH)\cdot CH_2\cdot CO_2Et,$$

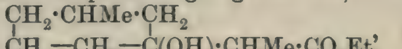
produced by the influence of zinc on β-methyl*cyclo*pentanone and ethyl bromoacetate, boils at 115—120° under 12 mm. pressure; the *methyl* ester boils at 110—115° under 12 mm. pressure. The unsaturated *ester*, $C_6H_8Me\cdot CO_2Et$, prepared by the action of potassium hydrogen sulphate, boils at 88—91° under 15 mm. pressure.

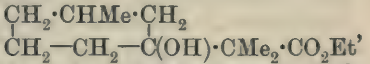
*2-Methyl-5-*iso*propylphenylacetic acid*, $C_6H_3MePr^{\beta}\cdot CH_2\cdot CO_2H$, melts at 69—70°, and boils at 180—183° under 15 mm. pressure; cold fuming nitric acid converts it into the *dinitro*-derivative, $C_{12}H_{14}O_6N_2$, which crystallises from dilute methyl alcohol in white leaflets and melts at 196—197°. The *ethyl* ester, obtained from carvone and ethyl bromoacetate, boils at 155° under 15 mm. pressure.

Dihydrocarveolacetic acid, $OH\cdot C_{10}H_{16}\cdot CH_2\cdot CO_2H$, boils at 196—208° under 14 mm. pressure, and when distilled under atmospheric pressure yields an unsaturated hydrocarbon, which should be homolimonene; the *ethyl* ester, prepared from dihydrocarvone and ethyl bromoacetate, boils at 150—170° and 282—288° under pressures of

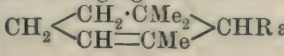
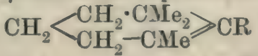
14 mm. and 760 mm. respectively, has a sp. gr. 0·997, and n_D 1·47664 at 20°.

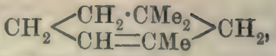
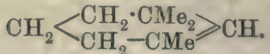
[With LEIMBACH].—*Thujoleacetic acid*, $OH{\cdot}C_{10}H_{16}{\cdot}CH_2{\cdot}CO_2H$, crystallises from a mixture of benzene and petroleum in leaflets, and melts at 90—91°; the *ethyl* ester, prepared from thujone and ethyl bromoacetate, boils at 154—164° under 14 mm. pressure. Iso*thujoleacetic acid* melts at 168—170°. M. O. F.

Condensation of Methylhexanone with Ethyl α-Bromopropionate and Ethyl α-Bromo*iso*butyrate. By JULIUS VON BRAUN (*Annalen*, 1900, **314**, 168—177. Compare foregoing abstract).—*Ethyl methyl*cyclo*hexanolpropionate*,  $\begin{array}{l}\mathrm{CH_2{\cdot}CHMe{\cdot}CH_2}\\ \mathrm{CH_2{-}CH_2{-}C(OH){\cdot}CHMe{\cdot}CO_2Et}\end{array}$, prepared by the action of zinc on methyl*cyclo*hexanone and ethyl α-bromopropionate, boils at 128—133° under 8 mm. pressure; hydrolysis does not yield the acid, but gives rise to a mixture of methyl*cyclo*hexanone, methyl*cyclo*hexanol, and propionic acid.

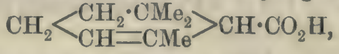
*Ethyl methyl*cyclo*hexanol*iso*butyrate*,  $\begin{array}{l}\mathrm{CH_2{\cdot}CHMe{\cdot}CH_2}\\ \mathrm{CH_2{-}CH_2{-}C(OH){\cdot}CMe_2{\cdot}CO_2Et}\end{array}$, obtained from methyl*cyclo*hexanone and ethyl α-bromo*iso*butyrate, boils at 134—139° under 10 mm. pressure; sodium ethoxide resolves it into methyl*cyclo*hexanone and butyric acid. When the hydroxy-ester is heated with potassium hydrogen sulphate at 150—160°, the unsaturated *ester*, $C_{13}H_{22}O_2$, is produced, boiling at 116° under 8 mm. pressure; the acid from this compound, when heated under the ordinary pressure, yields the *hydrocarbon*, $C_{10}H_{18}$, which must be a menthene of the meta-series. M. O. F.

Compounds of the *cyclo*Citral Series. By FERDINAND TIEMANN [and R. SCHMIDT] (*Ber.*, 1900, **33**, 3703—3710).—The conversion of the open chain ketone, ψ-ionone, into the *cyclo*citral derivative, ionone, by the agency of acids (Tiemann and Krüger, Abstr., 1894, i, 82) is now recognised as a change undergone by all compounds of the citral series. Further investigation of ionone has shown that this substance is a mixture of two isomerides, α- and β-ionones, which do not correspond with isomeric ψ-ionones.

In the following papers, to which the present communication is an introduction, the isomerism of the two modifications is proved to be dependent on the position of the unsaturated linking; it is also found that the production of two isomeric *cyclo*citrals characterises the action of acids on other members of the citral group. The constitution of *cyclo*citrals belonging to the α- and β-series is represented by the formulæ  $\mathrm{CH_2}<\begin{matrix}\mathrm{CH_2{\cdot}CMe_2}\\ \mathrm{CH{=}CMe}\end{matrix}>\mathrm{CHR}$ and  $\mathrm{CH_2}<\begin{matrix}\mathrm{CH_2{\cdot}CMe_2}\\ \mathrm{CH_2{-}CMe}\end{matrix}\gg\mathrm{CR}$ respectively. M. O. F.

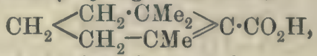
Inversion of Compounds belonging to the Citral Series. By FERDINAND TIEMANN [with R. SCHMIDT] (*Ber.*, 1900, **33**, 3710—3713). —The inversion of geraniolene is effected in three days by continued agitation with 65 per cent. sulphuric acid. The *cyclo*geraniolene boils between 130° and 140°, the major portion distilling at 138° (uncorr.), and when oxidised with potassium permanganate yields *iso*geronic acid, derived from the *a-cyclo*geraniolene,  $CH_2<\begin{matrix}CH_2\cdot CMe_2\\ CH{=}CMe\end{matrix}>CH_2$, and geronic acid from *β-cyclo*geraniolene,  $CH_2<\begin{matrix}CH_2\cdot CMe_2\\ CH_2{-}CMe\end{matrix}>CH$.

Geranic acid is converted likewise into *a-cyclo*geranic acid,



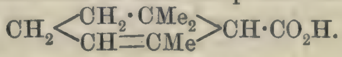
$$CH_2<\begin{matrix}CH_2\cdot CMe_2\\ CH{=}CMe\end{matrix}>CH\cdot CO_2H,$$

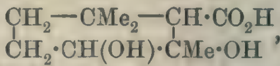
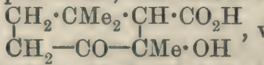
which melts at 106°, and *β-cyclo*geranic acid,



$$CH_2<\begin{matrix}CH_2\cdot CMe_2\\ CH_2{-}CMe\end{matrix}>C\cdot CO_2H,$$

which has not been yet obtained in crystals. M. O. F.

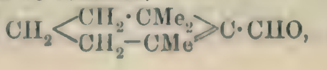
Constitution of *a-cyclo*Geranic Acid. By FERDINAND TIEMANN and HERMANN TIGGES (*Ber.*, 1900, 33, 3713—3719).—The *iso*geranic acid of Tiemann and Semmler (Abstr., 1894, i, 85), which melts at 106°, will be called *a-cyclo*geranic acid, in order to distinguish it from the aliphatic *iso*geranic acid (Tiemann, Abstr., 1900, i, 275) and from the *β-cyclo*geranic acid which corresponds with *β*-ionone. Experiments on the oxidation of this compound have shown that it has the constitution  $CH_2<\begin{matrix}CH_2\cdot CMe_2\\ CH{=}CMe\end{matrix}>CH\cdot CO_2H$.

*Dihydroxydihydro*cyclo*geranic acid*,  $\begin{matrix}CH_2{-}CMe_2{-}CH\cdot CO_2H\\ CH_2\cdot CH(OH)\cdot CMe\cdot OH\end{matrix}$, produced on oxidising *a-cyclo*geranic acid with potassium permanganate (Tiemann and Semmler, *loc. cit.*), melts at 198—200°; the *ethyl* ester crystallises from petroleum, and melts at 92°. *Hydroxyketodihydro*cyclo*geranic acid*,  $\begin{matrix}CH_2\cdot CMe_2\cdot CH\cdot CO_2H\\ CH_2{-}CO{-}CMe\cdot OH\end{matrix}$, which is also formed, crystallises from water or from ethyl acetate and petroleum in prisms melting at 145°; the semicarbazone melts at 216°.

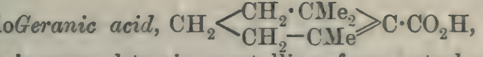
*iso*Geronic (4-dimethylheptan-6-onoic) acid (compare Tiemann and Schmidt, Abstr., 1898, i, 377), produced when the dihydroxy- and ketohydroxy-acids are oxidised with chromic acid, yields the semicarbazone melting at 198°.

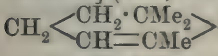
The *hydrogen ethyl* salt of *a*-acetyl-*ββ*-dimethyladipic acid, $CO_2Et\cdot CHAc\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CO_2H$, prepared by oxidising ethyl dihydroxydihydro*cyclo*geranate with chromic acid, is an oil; the *semicarbazone* crystallises from absolute alcohol and melts at 157°. When this ester is heated with aqueous potassium hydroxide in a reflux apparatus, it undergoes the ketone hydrolysis, yielding *iso*geronic acid, $COMe\cdot CH_2\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CO_2H$. M. O. F.

cycloCitral. By FERDINAND TIEMANN [with R. SCHMIDT] (*Ber.*, 1900, 33, 3719—3725).—Although compounds of the citral series, $CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}CHR$, give rise to the *cyclo*citrals by union of the carbon atoms in positions 1 and 6, citral itself is converted into cymene. If, however, the sensitive aldehyde group is protected, as in citralidenecyanoacetic acid (Tiemann, Abstr., 1900, i, 331), the normal cyclic product can be obtained.

β-cyclo*Citral*,  $CH_2<\begin{matrix}CH_2\cdot CMe_2\\ CH_2{-}CMe\end{matrix}>C\cdot CHO$, obtained by inverting

a and *b* citralidenecyanoacetic acids, and hydrolysing the *cyclo*-acids produced, is nearly colourless, has the odour of carvone, and boils at 88—91° and 95—100° under pressures of 10 mm. and 15 mm. respectively; it has sp. gr. 0·959 and 0·957 at 15° and 20° respectively, and n_D 1·49715 at 15°. The *semicarbazone* crystallises from methyl alcohol in large, transparent prisms containing the solvent, and melting at 165—166°; boiling ethyl acetate deposits it in thin leaflets melting at 166—167°. The additive *compound* of semicarbazide and *cyclo*citral, having the composition $C_{11}H_{21}O_2N_3$, instead of $C_{11}H_{19}ON_3$, crystallises from a mixture of ethyl acetate and benzene in slender needles, and decomposes at 250°. β-*cyclo*Citral yields β-ionone when condensed with acetone.

β-cyclo*Geranic acid*,  $CH_2{<}\genfrac{}{}{0pt}{}{CH_2\cdot CMe_2}{CH_2-CMe}{>}C\cdot CO_2H$, formed when the aldehyde is exposed to air, crystallises from petroleum in large, transparent prisms or plates, and melts at 93—94°; it decolorises bromine very slowly, yielding hydrogen bromide. Oxidation with alkaline permanganate gives rise to the *hydroxy-acid*, $C_{10}H_{16}O_3$, which melts and decomposes at 186°, and the *keto-acid*, $C_9H_{12}O_3$, which melts at 189°, and yields a *semicarbazone* melting at 240°; the main product of oxidation is *aa*-dimethylglutaric acid. M. O. F.

Constitution of α-Ionone. By Ferdinand Tiemann [and R. Schmidt] (*Ber.*, 1900, **33**, 3726—3727).—The constitutional formula,  $CH_2{<}\genfrac{}{}{0pt}{}{CH_2\cdot CMe_2}{CH=CMe}{>}CH{:}CH\cdot COMe$, for α-ionone is established by converting the ketone into *iso*geronic acid under the influence of ice-cold potassium permanganate followed by chromic acid. M. O. F.

Constituents of West Indian Sandalwood Oil. II. By Hugo von Soden and Wilhelm Rojahn (*Chem. Centr.*, 1900, ii, 1274—1275; from *Pharm. Zeit.*, **45**, 878. Compare Abstr., 1900, i, 401).—Attempts to separate amyrol into two components by fractionally distilling in a vacuum have shown that it probably consists of two secondary or tertiary sesquiterpene alcohols. Of these the *alcohol*, $C_{15}H_{25}\cdot OH$, of higher boiling point, present in the larger proportion, is a very viscous liquid, boils at 299°, has a sp. gr. of about 0·987 at 15°, and a rotation of about +36°. The second alcohol has not been isolated in a pure state, but appears to have the composition $C_{15}H_{23}\cdot OH$, and to be optically inactive.

From West Indian sandalwood oil, 0·1 per cent. of *amyrolin*, $C_{14}H_{12}O_3$, has also been isolated; it crystallises from methyl alcohol in stout crystals, is colourless, odourless, and tasteless, melts at 117°, and dissolves in hot alcohol or in alcoholic potash, giving in the former case a solution with a blue and in the latter a solution with a yellowish-green fluorescence. By the action of bromine in glacial acetic acid, a soluble and an insoluble product are formed. The latter is probably a *dibromide*, $C_{14}H_{12}Br_2O_3$; it is a white powder and melts at 157—159°. Amyrolin appears to be an aromatic compound of the character of a lactone. E. W. W.

Oil of Sweet Orange. By KARL STEPHAN (*J. pr. Chem.*, 1900, [ii], 62, 523—535).—The author has investigated the constituents of a large sample of the essential oil of sweet orange-peel which possessed the following characters: sp. gr. 0·851 at 15°; $[\alpha]_D$ +96°3′ at 20°; n_D 1·47245 at 20°; the residue left on evaporation amounted to 2·29 per cent.

After the removal of the terpenes by fractional distillation under 14 mm. pressure, the residual oil was shaken with sodium hydrogen sulphite solution; by this means, *n*-decaldehyde was separated, which boils at 93—94° under 12 mm. and at 207—209° under 755 mm. pressure, has a sp. gr. 0·828 at 15° and n_D 1·42977 at 15°. When *n*-decaldehyde is treated with β-naphthylamine and pyruvic acid, a substituted naphthacinchonic *acid*, $C_{23}H_{27}O_2N$, is obtained, which crystallises in white needles and melts at 237°. *n*-Decoic acid is produced when *n*-decaldehyde is oxidised with silver oxide; it has a sp. gr. 0·895 at 30° and 0·889 at 37°, and n_D 1·43078 at 30°. The author was unable to confirm the statements of Semmler (Abstr., 1891, 539) and Parry (*Chemist and Druggist*, 1900, 462, 722) that the oil contains citral, or that of Flatau and Labbé (Abstr., 1899, i, 422) that a small proportion of citronellal is present.

The oil remaining from the bisulphite treatment, when hydrolysed with alcoholic potassium hydroxide, yielded *n*-octoic acid. The alcohols were dried and treated with phthalic anhydride; an ester was produced which on hydrolysis furnished *n*-nonyl alcohol of sp. gr. 0·840 at 15° and n_D 1·43582 at 15°. The portion which was not converted into an ester was carefully fractionated under 22 mm. pressure; *d*-linalool (coriandrol) was found in the earlier fractions, whilst the later fractions consisted of *d*-terpineol which gave $[\alpha]_D$ +95°9′. *d*-Terpineol yields a nitrosochloride which is converted by piperidine into the terpenylnitrolpiperidine melting at 159°; it also combines with phenylcarbimide with formation of terpenylphenylurethane. The alcohol obtained by Wright (*Annalen*, 1884, **227**, 289) and supposed to be myristicol is *d*-terpineol.

The residue is a waxy mass which melts at 67—68° and gives a saponification number 65; it yields on hydrolysis a solid, saturated *acid*, $C_{27}H_{54}O_2$, melting at 77—78°, and an oil which solidifies on cooling, and melts at 138°; the latter substance gives Liebermann's cholesterol reaction, and appears to be related to phytosterol. When the residue is left for several days with warm sulphuric acid (32 per cent.), a *substance* separates in yellow crystals which melts at 192—193°, and contains 6·9 per cent. of sulphur.

The quantitative composition of the oil is as follows: terpenes, 96 per cent.; compounds containing oxygen, 1 per cent.; residue, 3 per cent. The compounds containing oxygen consist of *n*-decaldehyde, 5·7 per cent.; ester ($C_{10}H_{17}O_2C_8H_{15}$), 8·5 per cent.; nonyl alcohol, 7·0 per cent.; *d*-terpineol, 39·4 per cent.; and *d*-linalool, 39·4 per cent.

E. G.

Ononin. By FRANZ VON HEMMELMAYR (*Ber.*, 1901, **33**, 3538—3540. Compare Hlasiwetz, *J. pr. Chem.*, 1855, **65**, 419).—Onospin has the formula $C_{28}H_{32}O_{12}$, and its melting point is 172°, not 162° as given by Hlasiwetz.

On subjecting onospin to acid hydrolysis in the mode recommended by Hlasiwetz, an impure product is obtained melting indefinitely at 140—150°. After several crystallisations from dilute alcohol and subsequent extraction with water, a compound is obtained in white, glistening needles melting at 122°, but in quantity too small for analysis. The portion undissolved by water, after repeated extraction, yields a mixture of two substances, one in the form of long, flat needles melting at 155—157°, the other in white leaflets melting at 158—160°. The former, on analysis, gave numbers almost identical with those found by Hlasiwetz for his ononetin, so that the crude material is probably a mixture of isomerides $(C_{11}H_{10}O_3)_n$. In accordance with the above formula for onospin, its hydrolysis may be represented by the equation $C_{28}H_{32}O_{12} = C_{22}H_{20}O_6 + C_6H_{12}O_6$. A. L.

Sugars of Xanthorhamnin and Quercitrin. By Emil Votoček and V. Frič (*Zeit. Zuckerind. Böhm.*, 1900, **25**, 1—7).—Besides rhamnose, xanthorhamnin yields galactose on hydrolysis, the ratio between the quantities of the two sugars obtained being 2 mols. of anhydrous rhamnose to 1 mol. of galactose. Quercitrin yields no sugar but rhamnose on hydrolysis. T. H. P.

Conversion of Hyoscyamine into Atropine by means of Sodium Alkyloxides in Alcoholic Solution. By Arrigo Mazzucchelli (*Gazzetta*, 1900, **30**, ii, 476—487).—The conversion of hyoscyamine into atropine by means of (1) a methyl alcohol solution of sodium methoxide, (2) sodium ethoxide in ethyl alcohol, (3) an alcoholic solution of sodium hydroxide, and (4) sodium propoxide in propyl alcohol, has been studied. The mean values of K for the various cases are (1) 0·001295, (2) 0·00788, (3) 0·00764, and (4) 0·0114. Solution (2), prepared by dissolving sodium in absolute alcohol, and solution (3), obtained by dissolving carefully dehydrated sodium hydroxide in absolute alcohol, show identical behaviour. The energy of the sodium alkyloxides, as given by the velocity with which they convert hyoscyamine into atropine, does not appear to depend on the extent to which they are electrolytically dissociated, as the transformation proceeds most quickly in the solvent having the smallest ionising power. T. H. P.

Action of Ethyl Iodide on Caffeine. By A. I. Rossolimo (*J. Russ. Phys. Chem. Soc.*, 1900, **32**, 727—732).—*Caffeine ethiodide*, $C_8H_{10}O_2N_4$,EtI, prepared by heating caffeine with excess of ethyl iodide in a sealed tube at 160—170° for 20 hours, separates from absolute alcohol in short, pale yellow, acicular crystals which melt with evolution of gas at 182—183°, have a bitter taste, and are readily soluble in water, which, however, quickly decomposes them.

Caffeine ethochloride, formed on heating an alcoholic solution of the iodide with an excess of freshly precipitated silver chloride, crystallises from alcohol in colourless, transparent, superposed plates or from a mixture of alcohol and benzene in thin, silky, white rods melting at 182—183°. Its *platinichloride* is precipitated as an orange powder composed of microscopic acicular crystals which readily decompose on heating. The *aurichloride* separates from alcohol in microscopic, lemon-yellow, acicular crystals melting at 188°. T. H. P.

Action of Bromine on Cinchonidine. Two Isomeric α-and β-Dibromocinchonidines. By J. GALIMARD (*Bull. Soc. Chim.*, 1901, [iii], 25, 84—88).—When cinchonidine sulphate is heated with fuming hydrobromic acid and the liquid subsequently neutralised with ammonia, or sodium carbonate, cinchonidine hydrobromide, $C_{19}H_{22}ON_2,HBr$, is precipitated as a nearly white powder which is very soluble in hot alcohol, but insoluble in water or ether.

When cinchonidine sulphate is warmed with bromine in dilute hydrobromic acid solution and the liquid left to cool, *α-dibromocinchonidine hydromide*, $C_{19}H_{20}Br_2ON_2,2HBr$, crystallises out in colourless needles, which melt and decompose at 205—206°. When treated with ammonia or sodium carbonate, it yields *α-dibromocinchonidine*, which decomposes without melting at 180°. One of the atoms of bromine in α-dibromocinchonidine has probably replaced the hydrogen of a hydroxyl group, since it is readily removed by boiling with water or alkalis, or by the action of silver nitrate.

α-Dibromocinchonidine is unstable, and on keeping, or when treated with nitric acid, it is converted into the isomeric *β-dibromocinchonidine*. α-Dibromocinchonidine hydrobromide also, when subjected to prolonged boiling with alcohol, yields more highly brominated compounds, including a mixed hydrobromide of dibromocinchonidine and tribromocinchonidine, $C_{19}H_{20}ON_2Br_2,C_{19}H_{19}ON_2Br_3,HBr$, which, on treatment with lime, is converted into β-dibromocinchonidine. This base forms colourless crystals decomposing at 200° without melting, and is lævorotatory; bromine is not removed from it by treatment with aqueous alkalis or by silver nitrate.

N. L.

The Formula of Cotarnine. By ARTHUR HANTZSCH (*Ber.*, 1900, 33, 3685—3686).—A reply to Decker (Abstr., 1900, i, 683).

A. H.

2-Ethylpiperidine and its Properties. By ANDREAS LIPP (*Ber.*, 1900, 33, 3513—3519. Compare Ladenburg, Abstr., 1898, i, 339).—The compound obtained by the reduction of picolylalkine (compare Abstr. 1897, i, 230) is shown to be 2-ethylpiperidine. A number of

	2-Ethylpiperidine.		1-Methyl-2-ethylpiperidine.	
	Ladenburg.	Lipp.	Ladenburg.	Lipp.
Boiling point ……	141—143°	142—143° corr. at 719 mm.	150—151·5°	153·5—154·5° at 730 mm.
Sp. gr. at 0° ……	0·8666	0·8651	0·8515	0·8541
Hydrochloride……	m. p. 178—181°	181—182°		153—154°
Platinichloride …	m. p. 189°, decomposes at 191°	melts and decomposes at 208—210°	not obtained crystalline	crystalline
Aurichloride ……	m. p. 129—130°	129—130°	122—123°	118—119°
Mercuric chloride.				202—205°

derivatives have been prepared and investigated, but the properties of these differ only slightly from those given by Ladenburg. J. J. S.

***d*- and *l*-2-Ethylpiperidine.** By HANS FRESE (*Ber.*, 1900, **33**, 3483—3484).—The author corrects the values for the physical constants of *d*- and *l*-2-ethylpiperidine formerly given by Ladenburg (*Annalen*, 1888, **247**, 71). The pure *d*-tartrate melts at 105·5°, and yields a base which distils at 142—143·5° and has a sp. gr. 0·8680 at 4°; $[\alpha]_D + 17{\cdot}5°$. The *l*-tartrate was not obtained pure; the derived base boils at 138—142° and has $[\alpha]_D - 14{\cdot}55°$. W. A. D.

The Occurrence of Intermediate Products in the Synthesis of Pyrroles from 1 : 4-Diketones. By LUDWIG KNORR and PAUL RABE (*Ber.*, 1900, **33**, 3801—3803).—When ethyl *β*-diacetylsuccinate is treated with dry ammonia gas at 0° in the presence of ether, it dissolves and the solution then deposits ethyl *β*-amino-*β*-hexene-*ε*-one-*γδ*-dicarboxylate, $NH_2\cdot CMe\colon C(CO_2Et)\cdot CHAc\cdot CO_2Et$, in compact, well-developed crystals. This substance gradually loses the elements of water when it is preserved, and passes into ethyl 2 : 5-dimethylpyrrole-3 : 4-dicarboxylate, a change which also occurs when it is dissolved in acetic acid, hot alcohol, or dilute mineral acids. The aminohexenone compound evolves ammonia when treated with concentrated aqueous soda and reacts with hydrazine hydrate to form bis-3-methylpyrazolone. Ethyl diacetylsuccinate therefore forms an intermediate aminoketone when treated with ammonia, and in this respect resembles the *αγ*-ketones and some of the *αε*-ketones, such as ethyl benzylideneacetoacetate. A. H.

Compounds of Bismuth Salts with Organic Bases. By CLEMENTE MONTEMARTINI (*Gazzetta*, 1900, **30**, ii, 493—494).—A preliminary note, published on account of the appearance of a paper by Hauser and Vanino (Abstr., 1900, i, 641).

On adding pyridine to an ethereal solution of bismuth chloride, a white precipitate is obtained, consisting of a double salt of 1 mol. of bismuth chloride with 1·5 mols. of pyridine. T. H. P.

Constitution of Platinum Bases. By SOFUS M. JÖRGENSEN (*Zeit. anorg. Chem.*, 1900, **25**, 353—377. Abstr., 1900, i, 542).—Several methods are described for the preparation of platopyridinetriammine chloride, $PtPy(NH_3)_3Cl_2,H_2O$. The salt crystallises in lustrous, white, rhombic tablets; when heated at 120—130°, it loses ammonia and pyridine and yields a bright yellow powder containing the compounds $Pt(NH_3)_2Cl_2$, $PtPyNH_3Cl$, and $PtPy_2Cl_2$; heated with hydrochloric acid on the water-bath, it yields the compound $PtPyNH_3Cl_2$ and platosammine chloride; with potassium platinochloride, it yields the *salt* $PtPyNH_3Cl_2,PtCl_2,H_2O$, which is very characteristic, crystallises in flat, crimson needles, and is decomposed by heating at 115°.

Anderson's salt, $PtPy_2Cl_4$, Balbiano's salt, and chloroplatinsemidipyridine chloride, when reduced with sodium thiosulphate, all yield the platopyridineammine chloride *α*, whereas the chloroplatinpyridine chloride, $PtPy_2Cl_4$, corresponding with Gerhardt's chloride, is not reduced by sodium thiosulphate, and when treated with hydrogen sulphide yields the platopyridineammine chloride *β*.

Ethylenediamine platinochloride, $PtC_2H_4(NH_2Cl)_2$, when heated with water on the water-bath, is converted into platosemidiethylenediamine chloride.

These reactions are in harmony with the view that Peyrone's chloride is the symmetrical compound, $Cl{\cdot}NH_3{\cdot}Pt{\cdot}NH_3{\cdot}Cl$, and Reiset's chloride the unsymmetrical compound, $Cl{\cdot}NH_3{\cdot}NH_3{\cdot}Pt{\cdot}Cl$. E. C. R.

Compounds of Metallic Salts with Bases of the Pyridine Series. By DANIEL TOMBECK (*Ann. Chim. Phys.*, 1900, [vii], **21**, 433—469. Compare this vol., i, 135).—The halogen salts of zinc and cadmium combine with two molecular proportions of the corresponding salts of the aromatic amines to form compounds of the type $ZnCl_2,2NH_3PhCl$; pyridine also forms an analogous derivative, $ZnCl_2,2C_5NH_6Cl$. Two mols. of a pyridine base unite with 1 mol. of a halogen salt of zinc or cadmium to form a salt of the type $CdCl_2,2C_6H_7N$, and the combination has been effected in the case of picoline, lutidine, and collidine. These bases also form similar compounds with silver bromide, iodide, and cyanide, but the chloride interacts only with picoline.

The connection between the dissociation pressures of these double compounds and the temperature has been studied; the results obtained are tabulated, and the paper also contains the corresponding dissociation pressure curves. G. T. M.

Action of Bromine on 3-Picoline. By E. DEHNEL (*Ber.*, 1900, **33**, 3498—3500).—A *monobromo*-derivative, $C_5NH_4{\cdot}CH_2Br$, is the principal product when 3-picoline is heated with bromine (2 mols.) and concentrated hydrochloric acid for 10 hours at 150°; the base was not isolated owing to its instability, but was converted into the *picrate*, which crystallises from benzene in rosettes of yellow needles, melts at 114°, and on boiling with water for 2 hours yields the *picrate* of 3-*picolylalkine* (3-*hydroxymethylpyridine*), $C_5NH_4{\cdot}CH_2{\cdot}OH$, in the form of long, yellow needles. The *base*, formed on decomposing this salt, could not be obtained pure, but the *aurichloride* forms small, yellow crystals melting at 136—137°, and the *platinichloride*, brownish-red plates melting at 193—195°.

More complex derivatives of 3-picoline were also formed in the bromination; on distilling in a vacuum, a liquid boiling at 40—50°, and a solid distilling at 90—100°, were isolated, both apparently having the composition $C_{12}H_{10}N_2Br_5$. W. A. D.

Hantzsch's Synthesis of Ethyl Dihydrocollidinedicarboxylate. By PAUL RABE and ADOLF BILLMANN (*Ber.*, 1900, **33**, 3806—3811. Compare this vol., i, 147).—Both the mono- and diethyl esters of ethylidenebisacetoacetic acid are converted by alcoholic ammonia at 0° into *ethyl β-amino-δ-methyl-β-heptene-ζ-one-γ : ε-dicarboxylate*, $NH_2{\cdot}CMe{:}C(CO_2Et){\cdot}CHMe{\cdot}CHAc{\cdot}CO_2Et$, which forms large, well-developed, non-fluorescent triclinic crystals melting at 140°. It is not affected by alkalis, and by phenylhydrazine is converted into the *phenylhydrazone* of *ethyl ethylidenebisacetoacetate*,

$$NHPh{\cdot}N{:}CMe{\cdot}CH(CO_2Et){\cdot}CHMe{\cdot}CHAc{\cdot}CO_2Et,$$

which crystallises in needles melting at about 203°. Ethyl dihydrocollidinedicarboxylate could not be obtained by the action of ammonia on ethyl ethylidenebisacetoacetate, and the statement of Knoevenagel and Klages (*Annalen*, 1894, **281**, 105) must therefore be inaccurate. This fact also shows that in Hantzsch's synthesis of ethyl dihydrocollidinedicarboxylate from ethyl acetoacetate and aldehyde ammonia, ethyl ethylidenebisacetoacetate cannot be formed as an intermediate product.

Ethyl methylenebisacetoacetate, on the other hand, as stated by Knoevenagel, readily forms ethyl dihydrolutidinedicarboxylate.

A. H.

o-Nitrophenyl-2-picolylalkine and its Derivatives; Phenyl-2-picolylalkine. By E. Roth (*Ber.*, 1900, **33**, 3476—3479).—o-*Nitrophenyl-2-picolylalkine* (*β-o-nitrophenyl-β-hydroxy-2-ethylpyridine*), $NO_2\cdot C_6H_4\cdot CH(OH)\cdot CH_2\cdot C_5NH_4$, obtained by heating 2-picoline with *o*-nitrobenzaldehyde and water for 7—8 hours at 137—140°, separates from dilute alcohol in snow-white crystals, melts at 137—138°, is not volatile with steam, and yields an *aurichloride* which forms prisms and melts at 155°; the *platinichloride* melts at 212°, the green *ferrocyanide* at 148° with decomposition, and the *picrate* at 161°. The *acetate*, $NO_2\cdot C_6H_4\cdot CH(OAc)\cdot CH_2\cdot C_5NH_4$, crystallises from alcohol and melts at 82°. o-*Aminophenyl-2-picolylalkine* (*β-o-aminophenyl-β-hydroxy-2-ethylpyridine*), obtained by reducing the nitro-compound with zinc or iron and hydrochloric acid, separates from alcohol as a snow-white mass which melts at 97—98°, and becomes red in the air; the *picrate*, *platinichloride*, and *ferrocyanide* were prepared.

Phenyl-2-picolylalkine (*β-phenyl-β-hydroxy-2-ethylpyridine*),

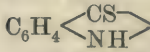
$$OH\cdot CHPh\cdot CH_2\cdot C_5NH_4,$$

obtained by heating 2-picoline with benzaldehyde and water for 10 hours at 135°, crystallises from dilute alcohol in white leaflets and melts at 96—97°; the *platinichloride*, with $3H_2O$, melts at 104°, the *aurichloride* at 131—132°, and the *mercurichloride* at 162°.

W. A. D.

2-Phenyl-6-stilbazole and 2-Phenyl-6-o-hydroxystilbazole. By E. Dehnel (*Ber.*, 1900, **33**, 3494—3497).—2-*Phenyl-6-stilbazole* (2-*phenyl-6-styrylpyridine*), $C_6H_5\cdot C_5NH_3\cdot CH\colon CHPh$, obtained by heating 2-methyl-6-phenylpyridine (Scholtz, Abstr., 1895, i, 562) with benzaldehyde for 5—6 hours at 250—260°, crystallises from dilute alcohol in beautiful, white needles and melts at 79°; the *hydrochloride*, with $4H_2O$, crystallises from dilute hydrochloric acid in long needles melting at 100°, and in yellow plates from alcohol or acetone. The *aurichloride* forms thick, red crystals and melts at 179°, and the *platinichloride* melts at 220°; the *zincochloride* forms yellow crystals. With bromine, the base yields the *compound* $C_{19}H_5NBr_4,HBr$, which forms rose-coloured, six-sided plates, melts at 172°, and, when boiled with alcohol, yields 2-*phenyl-6-stilbazole dibromide*, $C_5NH_3Ph\cdot CHBr\cdot CHPhBr$, in the form of lustrous, white leaflets melting at 190°; on reduction, the base gives rise to 2-*phenyl-6-stilbazoline*, $C_5NH_9Ph\cdot CH_2\cdot CH_2Ph$, which forms a non-crystallisable, white syrup, and yields a *hydrochloride* crystallising from water in stellar aggregates of white needles, which darken at 160° and decompose at 200°; the *platinichloride* melts at 155—156°.

2-Phenyl-6 : o-*hydroxystilbazole* (*2-phenyl*-6 : o-*hydroxystyrylpyridine*), $C_5NH_3Ph\cdot CH\colon CH\cdot C_6H_4\cdot OH$, obtained by heating salicylaldehyde with 2-phenyl-6-methylpyridine for 8—10 hours at 200°, crystallises from benzene in spherular aggregates of white needles and melts at 138°; the *hydrochloride* forms dark yellow needles and melts at 126—127°; the *aurichloride* brownish-red needles melting at 189°; the amorphous *platinichloride* melts at 190°. W. A. D.

Sulphur Derivatives of Aromatic Amines. By Albert Edinger (*Ber.*, 1900, **33**, 3769—3770).—This is a preliminary paper, occasioned by Gutbier's communication (this vol., i, 96). From acridine and flowers of sulphur *mesothioacridone* is obtained; this has, presumably, the constitution  $C_6H_4<\substack{CS\\NH}>C_6H_4$, and is analogous to Graebe's mesoacridone (Abstr., 1893, i, 650), from which it can be obtained by the action of phosphorus and sulphur at 260°. It crystallises in red needles and melts at 275°; phosphorus pentachloride converts it into Graebe's mesochloroacridine, phosphorus and bromine into *mesobromoacridine*, which melts at 119°, and forms *mesoiodoacridine*, melting at 169°, when it is treated with alcoholic sodium iodide. It dissolves in alkalis, and from the solution *benzyl* and *benzoyl* derivatives, $C_{13}H_8N\cdot S\cdot CH_2Ph$ and $C_{13}H_8N\cdot SBz$, can be prepared.

C. F. B.

3 : 3′-Dichlorobenzidine. By Paul Cohn (*Ber.*, 1901, **33**, 3551—3554).—3 : 3′-Dichlorobenzidine was made by reducing *o*-nitrochlorobenzene with zinc dust and sodium hydroxide and heating the resulting hydrazo-compound with strong hydrochloric acid; it is identical with the base prepared by chlorinating diacetylbenzidine (German Patents, 94410 and 97101). The *hydrochloride*, $C_{12}H_{10}N_2Cl_2,2HCl$, dissolves readily in alcohol, but is sparingly soluble in water; the latter statement is also true of the *sulphate*, *nitrate*, and *oxalate*. The *platinichloride* is unstable. The *dibenzoyl* derivative, $C_{12}H_6Cl_2(NHBz)_2$, crystallises from xylene in bundles of white needles and melts at 265°.

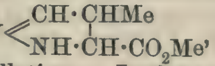
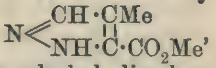
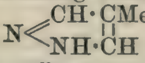
3 : 3′-Dichlorobenzidine yields a *tetrazo*-dye on uniting the diazotised substance with naphthionic acid; this has a bluish-red tint and its colour, unlike that of the simple congo red, is not altered by dilute acetic acid; it is best used in faintly acid baths. A. L.

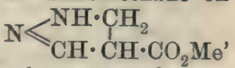
An Additive Reaction of Nitriles. By Alexander Eibner and Fr. A. Senf (*Ber.*, 1901, **33**, 3549—3551).—The capacity of the cyanohydrins of alkylideneamines to take part in condensations with aldehydes in presence of potassium cyanide or alcoholic potash appears to be general (compare von Miller and Plöchl, Abstr., 1896, i, 609) and extends to the cyanohydrins of hydrazones. With propylidenehydrazone cyanohydrin and benzaldehyde, the *substance*

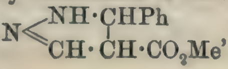
$$NHPh\cdot NH\cdot CHEt\cdot CO\cdot N\colon CHPh$$

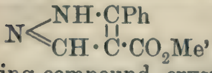
is formed; this separates from light petroleum in rhombic tablets and melts at 123°. In this instance, the best results are obtained when the two substances are allowed to remain together for 24 hours in alcoholic solution without any condensing agent. A. L.

Action of Methylacetylacetone and Ethylacetylacetone on Diazochlorides. By G. FAVREL (*Compt. rend.*, 1901, **132**, 41—42).—The action of methylacetylacetone on diazobenzene chloride yields a hydrazone, $\mathrm{NHPh\cdot N{:}CMe\cdot COMe}$, which melts at 134° and seems to be identical with the compound obtained by von Pechmann by the action of phenylhydrazine on diacetyl and by Japp and Klingemann by the action of diazobenzene chloride on methylacetoacetic acid. Ethylacetylacetone yields the corresponding ethyl derivative, which melts at 117° and was likewise prepared by Japp and Klingemann. Diazo-*o*-tolyl and diazo-*p*-tolyl chlorides behave in a similar manner, whilst the bisdiazochlorides from benzidine and its homologues yield the dihydrazones of diacetyl or propionylacetyl, as the case may be. *Diacetyldiphenyldihydrazone* melts at 283—284°, and the corresponding propionylacetyl compound at 265—268°. C. H. B.

Stereoisomerism of the two Crotonic Acids. 4-Methylpyrazole-5-carboxylic Acid. By HANS VON PECHMANN and EMIL BURKARD (*Ber.*, 1901, **33**, 3590—3594).—As in the interaction of methyl diazoacetate with methyl maleate and fumarate (Buchner, Abstr., 1893, i, 431), identical products are obtained by the action of diazomethane on the methyl esters of crotonic and *iso*crotonic acids. *Methyl 4-methylpyrazoline-5-carboxylate*,  $\mathrm{N}{<}\begin{matrix}\mathrm{CH\cdot CHMe}\\ \mathrm{NH\cdot CH\cdot CO_2Me}\end{matrix}$, is a colourless syrup which decomposes on distillation. It is oxidised by bromine to *methyl 4-methylpyrazole-5-carboxylate*,  $\mathrm{N}{<}\begin{matrix}\mathrm{CH\cdot CMe}\\ \mathrm{NH\cdot C\cdot CO_2Me}\end{matrix}$, which melts at 170—171°, crystallises from dilute alcohol, dissolves in most solvents, and in dilute alkalis and mineral acids, but not in acetic acid; the *ethyl* ester melts at 156—158°; the *acid*, $C_5H_6O_2N_2$, crystallises from water in small, glistening prisms, and melts at 218—220°. By distilling with soda-lime, the acid is converted into 4-methylpyrazole,  $\mathrm{N}{<}\begin{matrix}\mathrm{CH\cdot CMe}\\ \mathrm{NH\cdot CH}\end{matrix}$, which boils at 204—205° under 730 mm. pressure, and differs in odour and in solubility from 3-methylpyrazole; the double salt, with *silver nitrate*, crystallises from hot water in glistening needles, and melts at 142°, that of the isomeride melting at 121°; by the action of nitric acid, a yellow oil is produced, and not a crystalline nitro-compound; the *picrate*, like that of the isomeride, melts at 142°. T. M. L.

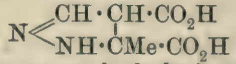
Pyrazole Derivatives from Diazomethane and Olefinemonocarboxylic Acids. By HANS VON PECHMANN and EMIL BURKARD (*Ber.*, 1901, **33**, 3594—3596).—By the action of diazomethane on methyl acrylate, methyl pyrazoline-3-carboxylate,  $\mathrm{N}{<}\begin{matrix}\mathrm{NH\cdot CH_2}\\ \mathrm{CH\cdot CH\cdot CO_2Me}\end{matrix}$, is produced, and on oxidation and hydrolysis is converted into Buchner and Papendieck's 3-pyrazolecarboxylic acid (Abstr., 1893, i, 431).

In a similar way, methyl cinnamate is converted into *methyl 5-phenylpyrazoline-4-carboxylate*,  $\mathrm{N}{<}\begin{matrix}\mathrm{NH\cdot CHPh}\\ \mathrm{CH\cdot CH\cdot CO_2Me}\end{matrix}$, which melts at 128°, crystallises in colourless prisms from alcohol, acetone, or benzene, and is insoluble in water. *Methyl 5-phenylpyrazole-4-carboxylate*,

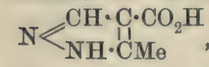


$N{<}\begin{array}{l}NH\cdot CPh\\ CH\cdot C\cdot CO_2Me\end{array}$, prepared by the action of bromine on the preceding compound, crystallises from alcohol in small prisms and melts at 188—190°; the acid is identical with the 5-phenylpyrazole-4-carboxylic acid described by Knorr (Abstr., 1895, i, 396), and decomposes at its melting point into carbon dioxide and 5-phenylpyrazole. T. M. L.

Combination of Diazomethane with Citraconic and Mesaconic Acids. By Hans von Pechmann and Emil Burkard (*Ber.*, 1901, 33, 3597—3598).—Esters of citraconic and mesaconic acids combine with diazomethane to form an ester of the same 5-methylpyrazoline-4 : 5-dicarboxylic acid,

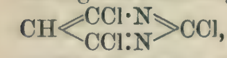


$N{<}\begin{array}{l}CH\cdot CH\cdot CO_2H\\ NH\cdot CMe\cdot CO_2H\end{array}$; by the action of bromine on this ester and subsequent hydrolysis, a mol. of carbon dioxide is eliminated, and 5-methylpyrazole-4-carboxylic acid,



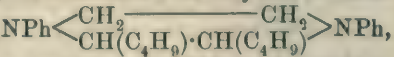
$N{<}\begin{array}{l}CH\cdot C\cdot CO_2H\\ NH\cdot CMe\end{array}$, is produced. T. M. L.

Pyrimidine from Barbituric Acid. By Siegmund Gabriel (*Ber.*, 1900, 33, 3666—3668. Compare Abstr., 1899, 638).—Pyrimidine can be prepared more readily than from methyluracil by treating barbituric acid (malonylureide) with phosphorus oxychloride and reducing the resulting trichloropyrimidine. 2 : 4 : 6-*Trichloropyrimidine*,

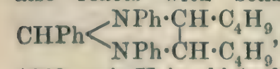


$CH{<}\begin{array}{l}CCl\cdot N\\ CCl:N\end{array}{>}CCl$, is a heavy, colourless oil the vapour of which attacks the eyes; it boils at 213° under 755 mm. pressure, and after solidification melts at 21°. When heated with zinc dust and water, it is converted into pyrimidine. The yield amounts to about 16 per cent. of that calculated from the barbituric acid. A. H.

Conversion of Anil Compounds of *iso*Valeraldehyde into A. W. von Hofmann's corresponding Alkyl-substituted Ethylene Bases. By Alexander Eibner and Georg Purucker (*Ber.*, 1900, 33, 3658—3664. Compare Abstr., 1892, 1189).—The base previously obtained by the reduction of *iso*valeraldehydeaniline with sodium and ethyl alcohol has the constitution of a di*iso*butylethyleneaniline, $C_4H_9\cdot CH(NHPh)\cdot CH(NHPh)\cdot C_4H_9$. It is not affected by boiling with concentrated hydrochloric acid, but condenses with ethylene bromide to form *diisobutyldiphenylpiperazine*,



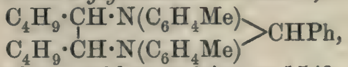
$NPh{<}\begin{array}{l}CH_2\text{———————}CH_2\\ CH(C_4H_9)\cdot CH(C_4H_9)\end{array}{>}NPh$, which crystallises in silky needles melting at 121°, and yields a p-*nitroso*-derivative crystallising in yellowish-green needles. The base also reacts with benzaldehyde to form a *glyoxaline* derivative,



$CHPh{<}\begin{array}{l}NPh\cdot CH\cdot C_4H_9\\ NPh\cdot CH\cdot C_4H_9\end{array}$, which separates in tabular crystals melting at 109°. *iso*Valeraldehyde-*p*-toluidine is also converted by reduction with sodium and ethyl alcohol into an *ethylene* base,

$$C_2H_2(C_4H_9)_2(NH\cdot C_6H_4Me)_2,$$

which is a thick, colourless oil boiling at about 270°. The *hydrochloride* crystallises in white plates, and the *diacetyl* derivative in vitreous monoclinic tablets melting at 138°, whilst the *monobenzoyl* derivative forms thin plates melting at 156°. The *dinitrosoamine*, $C_{24}H_{34}O_2N_4$, crystallises in pale yellow needles or cubes, melts at 92°, and is not affected by treatment with alcoholic hydrogen chloride. With benzaldehyde, the base forms a *glyoxaline* derivative,



$$\left.\begin{array}{l} C_4H_9\cdot \overset{}{C}H\cdot N(C_6H_4Me) \\ \quad\ \ | \\ C_4H_9\cdot CH\cdot N(C_6H_4Me) \end{array}\right> CHPh,$$

which crystallises in large tablets melting at 154°.

In the reduction of *iso*valeraldehydeaniline to di*iso*butylethyleneaniline, an intermediate product of the formula

$$NHPh\cdot CH(C_4H_9)\cdot NPh\cdot CH_2\cdot C_4H_9$$

is probably formed, and the mononitrile previously obtained by the action of dilute hydrocyanic acid on *iso*valeraldehydeaniline appears to be a derivative of this substance of the formula

$$NHPh\cdot CH(C_4H_9)\cdot NPh\cdot CH(C_4H_9)\cdot CN.$$

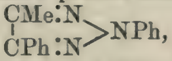
On reduction with sodium and ethyl alcohol, it yields the ethyleneaniline, whilst on distillation it yields the original base and the simpler nitrile. A. H.

1 : 3-Diphenyl-4-methylosotriazole. By Giacomo Ponzio and P. Rossi (*Gazzetta*, 1900, **30**, ii, 454—458).—This compound has been prepared by removing a molecule of acetic acid from the acetyl derivative of $\beta\alpha$-acetylbenzoylhydrazoxime by means of sodium carbonate.

The *acetyl* derivative of *acetylbenzoylhydrazoxime*,

$$NOAc\cdot CMe\cdot CPh\cdot N_2HPh,$$

crystallises from alcohol in faintly yellow prisms melting at 134·5°.

1 : 3-*Diphenyl*-4-*methylosotriazole*,  $\left.\begin{array}{l} CMe\colon N \\ | \\ CPh\colon N \end{array}\right> NPh$, separates from alcohol in almost colourless prisms melting at 37·5—38°, and is soluble in the cold in the ordinary organic solvents, but insoluble in water. The *dinitro*-derivative, $C_{15}H_{11}N_3(NO_2)_2$, crystallises from acetic acid in prisms melting at 230—231°. The *tetranitro*-compound separates from acetone in yellow prisms melting at 172°.

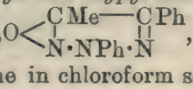
1-p-*Bromophenyl*-3-*phenyl*-4-*methylosotriazole*, $C_2N_3MePh\cdot C_6H_4Br$, crystallises from alcohol in slender, white needles melting at 97°.

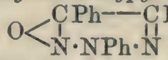
Acetylbenzoyl-p-*bromophenylhydrazoxime*,

$$NOH\colon CMe\cdot CPh\colon N_2H\cdot C_6H_4Br,$$

separates from alcohol in yellowish needles melting at 206—207°.

1-p-*Iodophenyl*-3-*phenyl*-4-*methylosotriazole* crystallises from alcohol in sparkling laminæ melting at 106°, and on treating with nitric acid yields the dinitrodiphenylmethylosotriazole melting at 230—231°. T. H. P.

Oxidation of Hydrazoximes. V. By Giacomo Ponzio (*Gazzetta*, 1900, **30**, ii, 459—465).—2-*Methyl*-3 : n-*diphenyl*-1 : 2-*oxypyrro*-1 : 4-*diazole* [4 : 5 *oxy*-1 : 3-*diphenyl*-4-*methylosotriazole*],  $O\left<\begin{array}{l} CMe—CPh \\ |\qquad\quad\ \ \| \\ N\cdot NPh\cdot N \end{array}\right.$, obtained by oxidising β : α-acetylbenzoylhydrazoxime in chloroform solution by means of mercuric oxide, crystallises from light petroleum in shining, faintly yellow needles melting at 83°, and is soluble in all ordinary organic solvents. It does not yield a hydrochloride when hydrogen chloride is passed through its ethereal solution, but on reduction either in alcoholic solution with zinc and hydrochloric acid, or with hydriodic acid in sealed tubes, it gives 1 : 3-diphenyl-4-methylosotriazole. Its *dinitro*-compound separates from acetic acid in microscopic, yellowish prisms melting at 260°, and is soluble in acetone, benzene, or chloroform.

Triphenyl-1 : 2-*oxypyrro*-1 : 4-*diazole* [4 : 5-*oxy*-1 : 3 : 4-*triphenylosotriazole*],  $\mathrm{O}<\begin{array}{l}\mathrm{CPh{-}{-}CPh}\\ \mathrm{N{\cdot}NPh{\cdot}N}\end{array}$, prepared by oxidising benzylhydrazoxime in chloroform solution with mercuric oxide, crystallises from acetone in aggregates of yellowish needles melting at 169°, and is soluble in benzene and slightly so in light petroleum or alcohol. By the action of zinc and hydrochloric acid in alcoholic solution, or of hydriodic acid in a sealed tube at 140°, it is converted into triphenylosotriazole, the *hexanitro*-compound of which, $C_{20}H_9N_3(NO_2)_6$, separates from acetic acid in shining, yellow prisms melting at 205—206°, and is almost insoluble in all other organic solvents. T. H. P.

6-Methylxanthine. By MARTIN KRÜGER (*Ber.*, 1900, 33, 3665. Compare Abstr., 1898, i, 699; 1899, ii, 233).—The 6-methylxanthine previously isolated from human urine readily yields theophylline (4 : 6-dimethylxanthine) on methylation, the latter being isolated by precipitating its sodium salt with sodium hydroxide in the cold. 6-Methylxanthine is best crystallised from acetic acid, and separates in very thin, six-sided, rhombic plates. A. H.

Azo-compounds Derived from *m*-Toluidine. By S. SAMELSON (*Ber.*, 1900, 33, 3479—3483).—The following azo-compounds were prepared by combining dimethyl-*m*-toluidine with diazotised bases. *Dimethyl*-m-*toluidineazobenzene*, $NMe_2{\cdot}C_6H_3Me{\cdot}N_2Ph$, obtained by using aniline, crystallises from alcohol in lustrous, bright-red needles, melts at 66°, and yields a dark-brown, amorphous *platinichloride*, which sinters at 200°, but does not melt at 280°.

The *sulphonic acid*, $NMe_2{\cdot}C_6H_3Me{\cdot}N_2{\cdot}C_6H_4{\cdot}SO_3H$, obtained with sulphanilic acid, is a reddish-brown, hygroscopic powder which is sparingly soluble in water, softens at 210°, carbonises at 225°, and yields a *barium* salt in the form of lustrous, brown crystals; on reduction, the acid gives sulphanilic acid and *p*-aminodimethyl-*m*-toluidine.

Dimethyl-m-*toluidine-azo*-p-*toluene*, $NMe_2{\cdot}C_6H_3Me{\cdot}N_2{\cdot}C_6H_4Me$, prepared with *p*-toluidine, crystallises from alcohol in lustrous, bright red needles, and melts at 121°; the *hydrochloride* crystallises from alcohol and melts at 172°; the *platinichloride* is a dark-red, amorphous powder, whilst the *sulphate* separates in greenish needles from methyl alcohol and melts at 201°.

Dimethyl-m-*toluidineazo*-m-*toluene*, $NMe_2{\cdot}C_6H_3Me{\cdot}N_2{\cdot}C_6H_4Me$, from *m*-toluidine, separates from alcohol in scarlet crystals, melts at 73—74°, and yields a brown, amorphous platinichloride which carbonises at 197°.

Dimethyl-m-*toluidineazo*-p-*phenetole*, obtained by using *p*-phenetidine, forms small, brown crystals and melts at 136—137°; the *platinichloride*, a bluish-grey, amorphous powder, carbonises at 197°.

Dimethyl-m-*toluidineazo*-p-*anisole*, separates from alcohol in reddish-brown crystals, melts at 135—136°, and yields a blue, crystalline *hydrochloride* melting at 164° which dissolves in alcohol to a red solution; the *sulphate* crystallises from methyl alcohol in dark blue needles and melts at 198°, and the *platinichloride* is amorphous and decomposes at 202°. W. A. D.

isoDiazotisation of Arylamines. By EUGEN BAMBERGER and ERNST RÜST (*Ber.*, 1900, **33**, 3511—3512. Compare Abstr., 1894, i, 511).—Aromatic bases, when diazotised in alkaline solution, that is, with amyl nitrite and sodium ethoxide, yield *iso*diazotates and no trace of the normal compounds. That the *iso*-compound is not a secondary product obtained by the action of sodium ethoxide on diazoaminobenzene has been proved by the fact that these compounds do not react on one another. Aniline, *o*- and *p*-toluidine, *p*-chloroaniline *p*-bromoaniline all react in a similar manner, but mesidine appears to be incapable of yielding an *iso*diazotate. Methylamine and benzylamine do not react, nor can phenylnitroamine be obtained by the action of amyl nitrate and sodium ethoxide on aniline. J. J. S.

Action of Nitrosobenzene on Aromatic Hydrazines. By EUGEN BAMBERGER (*Ber.*, 1900, **33**, 3508—3510. Compare Abstr., 1900, i, 193, and Spitzer, this vol., i, 98).—According to the author, molecular quantities of nitrosobenzene and *s*-diphenylhydrazine react in hot alcoholic solution to give a quantitative yield of azobenzene and β-phenylhydroxylamine. Nitrosobenzene and phenylhydrazine yield diazohydroxylaminobenzene and phenylhydroxylamine. *p*-Tolylhydrazine and nitrosobenzene give p-*toluenediazohydroxylaminobenzene*, $C_6H_4Me\cdot N{:}N\cdot NPh\cdot OH$, melting at 130—131° and phenylhydroxylamine, *p*-nitrosotoluene, and phenylhydrazine yield *benzenediazohydroxylamino*-p-*toluene*, $NPh{:}N\cdot N(OH)\cdot C_6H_4Me$, melting at 123·5—124° and *p*-tolylhydroxylamine. J. J. S.

Arylthiolsulphonates and Arylsulphinites of Diazo-compounds. By JULIUS TROEGER and ERICH EWERS (*J. pr. Chem.*, 1900, [ii], **62**, 369—430).—When benzidine or tolidine is diazotised, and the cold, neutral solution treated with a solution of the potassium salt of a thiolsulphonic acid, the corresponding thiolsulphonate of the diazo-compound is immediately precipitated. The products thus obtained sometimes undergo a remarkable transformation; for example, the benzene- and *p*-toluene-thiolsulphonates of bisdiazodiphenyl and bisdiazoditolyl separate in well-defined crystals which, when kept, lose their crystalline structure and become amorphous. The products obtained when diazo-compounds are treated with the salts of sulphinic acids are, however, always amorphous. The substances, both from thiolsulphonates and from sulphinites, are all of a golden- or orange-yellow colour. The thiolsulphonates cannot be purified by recrystallisation, since decomposition readily occurs with evolution of nitrogen; some of the products obtained with sulphinites dissolve in cold ethyl acetate or chloroform, and can be reprecipitated by means of light petroleum. When heated with aniline or nitrobenzene, solution of either series of compounds is effected with simultaneous evolution of the nitrogen, and this reaction has been employed for the estimation of the nitrogen. All the salts of diazo-compounds described in this paper yield a carmine red coloration with alcoholic potassium hydroxide.

By the action of thiolsulphonates on bisdiazodiphenyl chloride, the following salts were obtained. *Bisdiazodiphenyl dibenzenethiolsulphonate*, $C_{12}H_8(N_2\cdot S\cdot SO_2Ph)_2$, decomposes at 129—130°, the *di*-p-*toluenethiolsulphonate* at 147°, the *di*-o-*toluenethiolsulphonate* at 140°, and the *di*-*α*- and -*β*-*naphthalenethiolsulphonates* at 125° and 131—133° respectively.

The following compounds were prepared by the addition of thiolsulphonates to solution of bisdiazoditolyl chloride. *Bisdiazoditolyl dibenzenethiolsulphonate* decomposes at about 132°; of the *di*-o- and -p-*toluenethiolsulphonates*, the latter decomposes at 135—136°; *di*-*α*- and -*β*-*naphthalenethiolsulphonates* decompose at 108° and 112° respectively.

By the action of sulphinites on the diazo-compounds as well in acid as in neutral solution, the following sulphones were obtained: *diphenylsulphonebisdiazodiphenyl*, $C_{12}H_8(N_2\cdot SO_2Ph)_2$, and the corresponding *di*-o- and -p-*tolyl*-, *di*-*α*- and -*β*-*naphthyl*-, and the *dibromophenyl-sulphones*. *Diphenylsulphonebisdiazoditolyl* decomposes at 119°, the corresponding *di*-o- and -p-*tolylsulphones* decompose at 119° and 128°, and the *di*-*α*- and -*β*-*naphthylsulphones* at 130° and 128° respectively; the *dibromophenylsulphone* decomposes at 128°.

The arylthiolsulphonates of diazo-compounds, derived from primary amines, are comparatively stable and indifferent towards acids and alkalis. When kept, they sometimes decompose spontaneously with evolution of nitrogen; a similar decomposition occurs on heating. They react with alkaline phenol solutions with formation of oxyazo-compounds and the alkali salts of the thiolsulphonic acids. The thiolsulphonates of these diazo-compounds are nearly insoluble in water, but more or less soluble in alcohol, ether, chloroform, or carbon disulphide; as the substances dissolve, decomposition occurs, and hence the original products cannot be recovered from their solutions. The compounds are obtained both amorphous and crystalline; many solutions yield at first oily precipitates which gradually harden, whilst a further quantity afterwards separates in leaflets or needles; some products are at first crystalline and soluble in water, but after a time become amorphous and insoluble. The colour of these substances is yellow, orange, red, or brown.

The following compounds were prepared by the action of thiolsulphonates on diazobenzene chloride. *Diazobenzene benzenethiolsulphonate*, $Ph\cdot N_2\cdot S\cdot SO_2Ph$, decomposes at 75°; if its solution in carbon disulphide is treated with alcohol and evaporated by means of a current of air, a yellow, crystalline residue is obtained, which consists of a mixture of diazobenzenephenylsulphone and diazobenzene benzenethiolsulphonate. *Diazobenzene* p-*toluenethiolsulphonate* decomposes at 88—89°, the *α*-*naphthalenethiolsulphonate* melts and decomposes at 95—96°, and the *β*-*naphthalenethiolsulphonate* decomposes at 79—80°.

The following salts result from the action of thiolsulphonates on *p*-diazotoluene chloride. p-*Diazotoluene benzenethiolsulphonate*, $C_6H_4Me\cdot N_2\cdot S\cdot SO_2Ph$, melts and decomposes at 80°, the p-*toluenethiolsulphonate* decomposes at 93°, the *α*-*naphthalenethiolsulphonate* decomposes at 115°, and the *β*-*naphthalenethiolsulphonate* melts and decomposes at 92°.

o-*Diazotoluene benzenethiolsulphonate* melts at 52° and decomposes at about 55°; the p-*toluenethiolsulphonate* melts and decomposes at 79°; the *α-naphthalenethiolsulphonate* decomposes at 86·5°, and the *β-naphthalenethiolsulphonate* melts and decomposes at 92·5°.

The compounds obtained by the action of potassium benzene- and *p*-toluene-thiolsulphonates on *m*-diazo-xylene chloride are extremely unstable. m-*Diazo-xylene α-* and *β-naphthalenethiolsulphonates* melt and decompose at 98—99° and 87—88° respectively; both these compounds readily react with alkaline resorcinol with formation of *m*-xyleneazoresorcinol.

Diazo-ψ-cumene benzenethiolsulphonate, $C_6H_2Me_3{\cdot}N_2{\cdot}S{\cdot}SO_2Ph$, melts and decomposes at 73°, the p-*toluenethiolsulphonate* melts and decomposes at 87°, the *α-naphthalenethiolsulphonate* softens at 52—53°, and melts and decomposes at 90—91°, and the *β-naphthalenethiolsulphonate* decomposes at 85°; the last-mentioned compound reacts with alkaline resorcinol in the cold with formation of ψ-cumeneazoresorcinol, and when warmed with alkaline phenol solution yields ψ-cumeneazophenol.

α-Diazonaphthalene benzenethiolsulphonate, $C_{10}H_7{\cdot}N_2{\cdot}S{\cdot}SO_2Ph$, melts and decomposes at 90—91°, the p-*toluenethiolsulphonate* decomposes at 97°, and the *α-naphthalenethiolsulphonate* decomposes at 108°; the *β-naphthalenethiolsulphonate* melts and decomposes at 101—102°, and reacts with alkaline solution of resorcinol with formation of α-naphthaleneazoresorcinol.

β-Diazonaphthalene benzenethiolsulphonate decomposes at 87°; the p-*toluenethiolsulphonate* melts and decomposes at 104°; and the *α-naphthalenethiolsulphonate* decomposes at 115—116°; the *β-naphthalenethiolsulphonate* softens at 55°, decomposes at 95—96°, and reacts with alkaline solution of phenol with formation of β-naphthaleneazophenol.

o-*Chlorodiazobenzene benzenethiolsulphonate* melts and decomposes at 87—88°; the p-*toluenethiolsulphonate* decomposes at 89—90°; the α- and *β-naphthalenethiolsulphonates* are extremely unstable, and could not be obtained in a pure, dry state. The corresponding m- and p-*chloro*-compounds were prepared.

p-*Bromodiazobenzene benzenethiolsulphonate* decomposes at 99—100°; the p-*toluenethiolsulphonate* melts and decomposes at 111°; the *α-naphthalenethiolsulphonate* melts at 105—106°, and the *β-naphthalenethiolsulphonate* melts and decomposes at 108—109°

m-*Bromodiazobenzene benzenethiolsulphonate* melts at 60°, and decomposes at 80°; the p-*toluene-* and *α-* and *β-naphthalene-thiolsulphonates* could not be obtained in a pure, dry state.

p-*Nitrodiazobenzene benzenethiolsulphonate* melts and decomposes at 113°; the p-*toluenethiolsulphonate* melts and decomposes at 116°, and when warmed with alkaline solution of resorcinol yields *p*-nitrobenzeneazoresorcinol; the *α-naphthalenethiolsulphonate* decomposes at 58°, and the *β-naphthalenethiolsulphonate* melts and decomposes at 127°.

m-*Nitrodiazobenzene benzenethiolsulphonate* melts and decomposes at 109—110°; the p-*toluenethiolsulphonate* decomposes at 92—93; both the α- and *β-naphthalenethiolsulphonates* soften at 50° and decompose at 56—57°.

The thiolsulphonates of *o*-nitrodiazobenzene are very unstable; only the *α-naphthalenethiolsulphonate* could be obtained in a pure state.

p-*Diazoanisole benzenethiolsulphonate*, $OMe{\cdot}C_6H_4{\cdot}N_2{\cdot}S{\cdot}SO_2Ph$, melts at 70—71° and decomposes at 73°; the p-*toluenethiolsulphonate* melts and decomposes at 102—103°; the α-*naphthalenethiolsulphonate* melts and decomposes at 100—101°, and the β-*naphthalenethiolsulphonate* decomposes at 91·5°; the three last-mentioned substances react with alkaline solution of resorcinol, with formation of *p*-anisoleazoresorcinol.

o-*Diazoanisole benzenethiolsulphonate* melts and decomposes at 73°; the p-*toluenethiolsulphonate* melts and decomposes at 82°; the α-*naphthalenethiolsulphonate* melts and decomposes at 95—96°, and the β-*naphthalenethiolsulphonate* decomposes at 92°.

p-*Diazophenetole benzenethiolsulphonate*, $OEt·C_6H_4·N_2·S·SO_2Ph$, melts and decomposes at 81—82°; the p-*toluenethiolsulphonate* melts and decomposes at 116°; the α- and β-*naphthalenethiolsulphonates* melt and decompose at 121° and 122° respectively, and react with alkaline resorcinol solution with formation of *p* phenetoleazoresorcinol.

Diazoazobenzene benzenethiolsulphonate, $Ph·N_2·C_6H_4·N_2·S·SO_2Ph$, melts and decomposes at 120°; the p-*toluenethiolsulphonate* melts and decomposes at 114°, and the α- and β-*naphthalenethiolsulphonates* melt and decompose at 117·5° and 116·5° respectively.

The stability of the thiolsulphonates of the diazo-compounds is largely dependent on the nature and position of the substituting radicles in the benzene nucleus. Negative atoms or groups, such as Cl, Br, NO_2, increase the stability if they enter the para-position to the diazo-group, whilst, on the other hand, if they occupy the meta-position, the products are less stable. The thiolsulphonates of *m*-nitrodiazobenzene are less easily decomposed than those of *m*-chloro- and *m*-bromo-diazobenzene, for whilst the salts of *m*-nitrodiazobenzene could all be obtained in a pure, dry state, in the case of the *m*-chloro- and *m*-bromo-diazobenzene only the benzenethiolsulphonate could be prepared.

Among the ortho-compounds, the thiolsulphonates of *o*-nitrodiazobenzene are less stable than those of *o*-chlorodiazobenzene; the α-naphthalenethiolsulphonate of *o*-nitrodiazobenzene was with difficulty obtained in a pure state, and the product decomposed within 12 hours; the benzene- and *p*-toluene-thiolsulphonates of *o*-chlorodiazobenzene can be kept for months without change, whilst its naphthalenethiolsulphonates rapidly decompose.

The naphthalenethiolsulphonates of diazo-compounds substituted in the ortho- or meta-position by negative radicles are the most unstable, whilst the benzenethiolsulphonate is the most stable.

The entrance of a methyl group into the benzene nucleus of the diazo-compound increases the stability of the thiolsulphonate; the naphthalenethiolsulphonates of such compounds are more stable than the *p*-toluene- and benzene-thiolsulphonates; the thiolsulphonates of *p*-diazotoluene are all somewhat more stable than the corresponding diazobenzene compounds. The benzene- and *p*-toluene-thiolsulphonates of *o*-diazotoluene can only be obtained with difficulty, and rapidly decompose, whilst the α- and β-naphthalenethiolsulphonates are readily prepared in a pure state.

The thiolsulphonates of diazo-ψ-cumene can all be obtained pure, but the benzene- and *p*-toluene-thiolsulphonates are the least stable.

Since the thiolsulphonates of the diazo-compounds can, in many cases, be kept for months without change, they rather resemble the diazo-sulphones than the unstable diazo-chlorides, -nitrates, and -sulphates.

The behaviour of many of these compounds points to the existence of two modifications; for example, the β-naphthalenethiolsulphonate of *p*-diazotoluene, the *p*-toluenethiolsulphonate of α-diazonaphthalene, the benzenethiolsulphonate of β-diazonaphthalene, and the β-naphthalenethiolsulphonate of *p*-chlorodiazobenzene are for a short time after their formation soluble in water and crystalline, and on drying pass into insoluble, amorphous modifications. Many substances are at first crystalline, and become resinous when dry; for example, the α- and β-naphthalenethiolsulphonates of β-diazonaphthalene and *m*-chlorodiazobenzene; with some of the benzenethiolsulphonates of diazo-compounds containing a halogen in the meta- or ortho-position, this change takes place so rapidly that the formation of the crystalline modification can only be observed with difficulty. The existence of these two modifications can be explained by means of the stereoisomeric formulæ suggested by Hantzsch (Abstr., 1894, i, 455). E. G.

Proteids of the Thymus Gland. By CORNELIS A. PEKELHARING and HUISKAMP (*Proc. K. Acad. Amsterdam*, 1900, 3, 383—386).—Hammarsten has shown that fibrin cannot be regarded as a calcium compound of fibrinogen. This, however, does not alter the views held by the present authors regarding the nature of the fibrin-ferment; but recent work on the thymus proteids confirms it. Two nucleo-proteids can be separated from aqueous extracts of thymus. One of these (Lilienfeld's nucleo-histon) is quite insoluble, the other is incompletely soluble in water containing from 0·1 to 0·5 per cent. of calcium chloride; by increasing the amount of calcium salt, or by adding other neutral salts, both dissolve readily.

The precipitates produced from thymus extract by the addition of the necessary amount of calcium chloride are to be considered as calcium salts, in which the nucleo-proteid plays the part of an acid. By treatment of these compounds with potassium oxalate, the potassium compound of nucleo-proteid is formed. The potassium nucleo-proteid, like the sodium and ammonium compound, is soluble in water. The magnesium and barium compounds are insoluble in water, but dissolve in ammoniated water. All these compounds of nucleo-histon are precipitated by the addition of so much salt that the fluid contains 0·9 of sodium chloride, 1·13 of potassium chloride, 0·1 of calcium chloride, and 0·2 of magnesium sulphate per cent. respectively. Elementary analyses of the calcium compounds of the two nucleo-proteids gave the following percentages: Calcium nucleo-histon: C, 45·3; H, 6·5; N, 17·1; P, 3·75; S, 0·51; Ca, 1·34. Calcium nucleo-proteid: C, 49·8; H, 7·3; N, 15·9; P, 0·95; S, 1·19; Ca, 1·34.

Both these calcium proteids can act as fibrin-ferment, but this action is influenced by the amount of calcium salt in solution as well, being most effective in fibrin formation when the solution contains from 0·1 to 0·5 per cent. of calcium chloride. Beyond this, no coagulation occurs. Horne has previously shown that the chlorides of calcium, barium, and strontium, when present to an extent exceeding 0·5 per cent., hinder blood coagulation. The same is true for the fibrin-ferment prepared from blood. If fresh blood is mixed with calcium chloride, so that 1 per cent. of that salt is present, it remains fluid but clots on dilution, and clots best when the percentage amount of calcium salt in solution is 0·25 per cent., that is, in the strength in which the calcium nucleo-proteids are least soluble. W. D. H.

The Influence of Various Substances on the Crystallisation of Hæmoglobin. By STANISLAUS VON STEIN (*Virchow's Archiv*, 1900, **162**, 477—487).—The experiments were performed on the blood of the guinea-pig, and the author's Canada balsam method of preparing crystals was used. Various reagents, such as distilled water, sodium chloride, potassium chloride, &c., were added to the blood, and in all cases beyond a certain limit (the numbers are given in detail) the addition finally prevents crystallisation. An interesting point noticed is that, with a certain percentage addition of sodium and potassium salts, the crystals obtained are principally six-sided plates instead of tetrahedra. W. D. H.

Antipeptone and Amphopeptone. By MAX SIEGFRIED (*Ber.*, 1900, **33**, 3564—3568. Compare this vol., i, 57).—The greater part of the paper is a reply to Kutscher's criticisms (this vol., i, 108). Fibrin or Witte's peptone, digested with pepsin in the presence of hydrochloric or sulphuric acid, yields two monobasic *acids*, $C_{21}H_{34}O_9N_6$, and $C_{21}H_{36}O_{10}N_6$; these substances give the biuret reaction and are strongly acidic, yielding salts on boiling with zinc oxide or barium carbonate.

G. T. M.

Chemical Composition of the Brain Tissue. By EMIL WÖRNER and HANS THIERFELDER (*Zeit. physiol. Chem.*, 1900, **30**, 542—551).—The following substances have been obtained from brain tissue by extraction with a mixture of benzene and alcohol or chloroform and alcohol at 45—50°.

1. *Cerebron* ($C = 69·16$, $H = 11·54$ and $N = 1·76$ per cent.) separates first; it forms perfectly white characteristic amorphous, nodular masses, does not contain phosphorus, and is insoluble in water, but dissolves in most organic solvents; when heated in a capillary tube, it becomes moist at about 130° and melts at 209—212°. When warmed with 85 per cent. alcohol at 50°, the rounded masses become transformed into well-defined hexagonal plates; this transformation is accompanied by an addition of water. It forms an amorphous *bromo*-derivative, and when warmed with hydrochloric acid reduces Fehling's solution owing to the formation of galactose.

2. A compound containing 56·1—56·5 per cent. of carbon and melting and decomposing at about 270°. It is characterised by the property it possesses of melting when warmed with alcohol containing benzene.

3. A substance crystallising in rosettes of small needles and having all the appearance of "protagon"; it is probable that this is a mixture.

J. J. S.

Myrosin. By THOMAS BOKORNY (*Chem. Zeit.*, 1900, **24**, 817 and 832. Compare Abstr., 1900, ii, 746).—Some *Cruciferæ* contain both myrosin and potassium myronate (or a glucoside yielding allylthiocarbimide, others contain myrosin alone with no corresponding glucoside, whilst in some cases neither is present. No instance has as yet been observed of the occurrence of potassium myronate without myrosin; the statement of Spatzier (*Pr. Journ.*, 1893, 25) that this is the case with *Capsella bursa pastoris* (Shepherd's purse) is erroneous. Bussy (*Journ. Pharm.*, **26**, 39) prepared myrosin by extracting mustard seed with cold water, evaporating at 40° to a syrup, and repeatedly precipitating with alcohol; the author finds, however, that the activity of myrosin is destroyed by 50 per cent. aqueous alcohol, whilst on drying expressed radish-juice, even at 25°, no active ferment can be obtained.

The action of myrosin is destroyed by a 5 per cent. formaldehyde solution, but not by a 1 per cent. solution, whilst a solution of the strength 1 : 10,000 is fatal to protoplasm. The fermenting power of myrosin is destroyed by 1 per cent. sulphuric acid, 0·1 per cent. silver nitrate solution, or 0·1 per cent. mercuric chloride solution, whilst hydroxylamine is without action. In presence of water, the ferment loses its power at 70—75°, protoplasm under the same conditions being killed at 50—60°. T. H. P.

Sensitiveness of Enzymes; their relation to Protoplasm. By THOMAS BOKORNY (*Chem. Zeit.*, 1900, **24**, 1113—1114; 1136—1138). —A parallel is drawn between enzymes and the protoplasm of lower organisms with respect to the action on both of poisons, temperature, or strong illumination. Some facts are tabulated that illustrate the parallelism. C. F. B.

Action of Enzymes on Chromatophores and Dissolved Dyes. By C. J. KONING (*Chem. Centr.*, 1900, ii, 1279—1280; from *Pharm. Weekbl.*, 1900, No. 21, 23, 24).—The death of organisms resulting from the destruction of the protoplasm, but in which an enzyme still remains active, is named necrobiose. The change of colour of the dying leaves of *Isatis tinctoria* is due to the action of the enzyme isatase on isatan, which is an unstable indoxyl compound. In order to preserve the natural colour of plants, such as, for instance, *Campanula rotundifolia*, the plant must be heated at a higher temperature to insure necrose or the destruction of both protoplasm and enzyme. The enzymes may also act as catalytic agents and in cases of necrobiose the glucosides are often decomposed by the action of the enzymes. The action of the colouring matters which accompany chlorophyll is also described more particularly in reference to carotin and anthocyanin. E. W. W.

Vegetable Oxidases. By B. SLOWTZOFF (*Zeit. physiol. Chem.*, 1900, **31**, 227—234).—Laccase loses its activity at high temperatures; its action is proportional to the square root of its quantity. The amount of the product obtained is a function of the quantity of ferment, not of the quantity of the oxidisable substance. The action goes on best in the presence of a slightly alkaline reaction. In composition and reactions, laccase is a proteid; it is, however, not destroyed by acids or by peptic or pancreatic digestion. W. D. H.

Lipase, the Fat-splitting Enzyme, and the Reversibility of its Action. By J. H. Kastle and A. S. Loevenhart (*Amer. Chem. J.*, 1900, **24**, 491—525).—The authors have employed ethyl butyrate to determine the activity of solutions of lipase, since it is much more rapidly hydrolysed than fats by this enzyme. The most convenient source of lipase is the pancreas of the pig, but it can also be obtained from other tissues, the lipolytic activity of which stand in the following ratio: pancreas, 1·0; liver, 2·93; kidney, 0·50; submaxillary gland, 0·36. Since the liver of the pig showed such remarkable activity, it was compared with the livers of the ox, sheep, chicken, and duck; in a series of parallel experiments, the liver of the pig hydrolysed 8·66 per cent. of the ethyl butyrate employed, that of the sheep 4·77, that of the duck 2·70, that of the ox 2·20, and that of the chicken 1·95 per cent. The extract of the stomach of the pig was found to possess lipolytic activity in neutral solution, but was rendered permanently inactive by free hydrochloric acid in the quantity normally present in the gastric juice. Lipase also occurs in the small intestine of the pig, the mucous lining of which possesses a lipolytic activity equal to three-fourths of that of the fresh pancreas.

Lipase is much more stable than is usually supposed; it hydrolyses ethyl butyrate most rapidly at 40°, and at 65—70° the enzyme is destroyed. It is almost completely removed from its solutions by repeated filtration through paper. The behaviour of lipase towards ethyl formate, ethyl acetate, ethyl propionate, and ethyl butyrate was studied; it was found that the higher the molecular weight of the ester, the more readily is it hydrolysed by lipase, whilst the converse is true for the hydrolysis of esters by acids.

The effect of several of the commoner antiseptics on lipase was examined; it is shown that such substances as silver nitrate, mercuric chloride, salicylic acid, and osmic acid are much more detrimental than the more feeble antiseptic substances, such as toluene, chloroform, and thymol; sodium fluoride, hydrofluoric acid, and acids generally are particularly harmful.

The rate of hydrolysis, in the case of the extract of the pig's liver, is directly proportional to the concentration of the enzyme, but independent of the concentration of the ester; the reaction is not complete in ordinary circumstances, but if the extract of lipase is very concentrated and the ester present in only small quantity, the hydrolysis approaches completion. The velocity of the reaction is not constant, but diminishes as the hydrolysis proceeds.

The authors have found that the synthesis of ethyl butyrate from butyric acid and alcohol can be effected by means of lipase, thus proving that the hydrolysis of an ester by this enzyme is a reversible reaction. The paper concludes with a discussion of the relation of this fact to the absorption of fat in the animal organism and the translocation of fatty reserve materials in plants. E. G.

Ptyalin Activity. By T. Maszewski (*Zeit. physiol. Chem.*, 1900, **31**, 58—64).—In the first series of experiments, equal quantities of saliva, and equal *volumes* of starch paste, were taken, but the amount of starch in the paste was variable. The amount of sugar formed increased with the increase in the amount of starch.

In the second series, the volume of starch paste was the variable quantity. The amount of sugar formed increased with the volume of the starch solution.

In the third series, the volume of the saliva was the variable quantity. Here the amount of sugar formed hardly varied at all; there was often a slight decrease in the amount of sugar formed, never an increase.

In the light of such experiments, the faultiness of methods used for the estimation of enzymes is revealed. W. D. H.

Tannase. By AUG. FERNBACH (*Compt. rend.*, 1900, **131**, 1214—1215).—*Aspergillus niger*, a mould which plays an important part in the industrial processes of gallic fermentation, yields, when macerated with cold water, a solution which promotes the hydrolysis of tannin. This extract, when concentrated in a vacuum and treated as in Lintner's preparation of amylase, yields a grey powder containing the tannin ferment *tannase*. Tannin dissolved in 10 parts of water is completely hydrolysed by a solution of this enzyme; the course of the fermentation is readily followed by means of the polarimeter, the rotation of the solution becoming *nil* when the action is completed. The same transformation is effected by the action of a tannase solution, passed through a Chamberland filter, on a sterilised solution of tannin.

G. T. M.

Tannase; a Diastase decomposing Gallotannic Acid. By HENRI POTTEVIN (*Compt. rend.*, 1900, **131**, 1215—1217. Compare preceding abstract).—Spores of *Aspergillus niger* are cultivated at 30° in Raulin's liquid, containing tannin instead of sucrose, until the mycelium begins to fructify; the mould is then washed and macerated in the dark with chloroform and water, the extract being passed through a Chamberland filter. Sterilised solutions of tannin are completely hydrolysed by the filtrate, but no action takes place if the tannase is destroyed by heating the solution to boiling. Variable quantities of dextrose are produced, together with gallic acid, during fermentation. *Aspergillus niger*, cultivated in the ordinary Raulin's liquid, does not yield tannase unless the sugar of the solution is replaced by gallic acid or tannin.

Phenyl and methyl salicylates are hydrolysed by tannase, and since they have a constitution similar to that proposed by Schiff for digallic acid, these results go to confirm the suggested formula. Tannase also hydrolyses tannates such as gelatin tannate; the ferment is in all probability widely distributed in nature and has been found in sumach leaves; this accounts for the fact that gallic acid always accompanies tannin. G. T. M.

Zymase from Sterilised Yeast. By EDUARD BUCHNER (*Ber.*, 1900, **33**, 3307—3310. Compare Abstr., 1897, ii, 380).—Washed and pressed bottom yeast was dried for 3 or 4 hours at temperatures from 35° to 100° under 30 mm. pressure, and was then sterilised by heating in hydrogen for several hours at temperatures varying from 98° to 110°. The material thus obtained, which was incapable of development in beer wort, was mixed with glycerol and water, and ground with sand and kieselguhr. The juice expressed from this mass possessed active fermentative powers, 20 c.c. of it when mixed with 8 grams of cane sugar yielding, on the average, about 0·5 gram of carbon dioxide. Similar results were obtained with yeast dried in the air and then heated at 97° in a current of carbon dioxide. The author regards this result as decisive against the view that the fermentative powers of expressed yeast juice are due to the presence of fragments of living protoplasm in the juice, since, in his experiments, no living protoplasm could be present.

It was observed that thoroughly dried yeast was extremely difficult to sterilise, and sometimes withstood heating at 100° for 8 hours.

A. H.

Simple Experiment to illustrate the Action of Zymase. By Robert Albert (*Ber.*, 1900, **33**, 3775—3778).—Fresh brewery yeast is freed from water by pressing, and rubbed through a sieve into a mixture of absolute alcohol and ether (3 : 1). After 4—5 minutes, the liquid is poured off, the residue drained, washed with ether, and spread out in a thin layer on filter-paper to dry. A yellowish-white powder is obtained, which contains no live yeast cells, but ferments sugar solution vigorously.

The zymase is contained within the dead cells, and cannot be extracted with water directly. To obtain a fairly strong solution of it, the powder is rubbed with very fine quartz sand in a large mortar, water then added, and the mixture rubbed for 10 minutes more. It is then filtered with the aid of a pump through hardened filter-paper, some of the dilute zymase solution precipitated with alcohol and ether, the powder so obtained dissolved in a little water, a little kieselguhr added, and filtered. The clear filtrate so obtained ferments cane sugar almost instantaneously, even at the ordinary temperature.

C. F. B.

Invertase from Yeast. By Ernst Salkowski (*Zeit. physiol. Chem.*, 1900, **31**, 305—328. Compare Kölle, Abstr., 1900, i, 572).—Invertase obtained by Barth's method (*Ber.*, 1878, **11**, 474) always contains an appreciable amount of yeast-gum (Abstr., 1894, i, 222, 316; 1895, i, 166), which can be isolated in the form of its copper sodium derivative. Four different specimens examined contained from 17·17 to 65·3 per cent. of this gum. The gum, on hydrolysis, yields *d*-mannose (Hessenland), and this is probably the origin of the mannose obtained by Osborne and by Kölle from so-called invertase. Contact with alcohol appears to rapidly destroy the hydrolytic power of diastase. The isolation of "sucrase," the actual enzyme of cane sugar inversion from yeast in a pure form by any of the ordinary methods, appears to the author to be hopeless, on account of the large number of other enzymes present, namely, maltase, zymase, and the three enzymes previously described by him (*Zeit. physiol. Chem.*, 1889, **13**, 506).

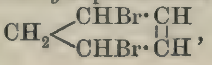
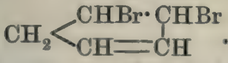
J. J. S.

Organic Chemistry.

Hydrogenation with Sodium and Alcohol. By ALBERT LADENBURG (*Ber.*, 1901, **34**, 200—201. Compare von Baeyer, *Ber.*, 1900, **33**, *Sonderheft*, p. 57).—A claim for priority in the use of sodium and alcohol for hydrogenation, as, for example, in the reduction of pyridine to piperidine. T. M. L.

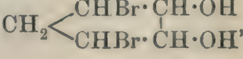
Hydrocarbon, C_6H_{10}, from Dimethylallylcarbinol. By EUGEN LJUBARSKY (*J. pr. Chem.*, 1900, **62**, [ii], 567—577).—The hydrocarbon, C_6H_{10}, first obtained by Saytzeff (Abstr., 1877, ii, 298) from dimethylallylcarbinol, is a colourless, mobile liquid which boils at 73—76°, exhibits a slight violet-blue fluorescence, and has the sp. gr. 0·71427 at 20°/0°, 0·71504 at 20°/20°, and 0·71415 at 20°/4°, and a molecular refraction 50·34. It absorbs oxygen from the air with formation of a thick, yellow oil. By the action of hypochlorous acid on the hydrocarbon, a pale yellow liquid, probably the dichlorohydrin, is obtained, which is converted by barium hydroxide into a thick, colourless liquid of the composition $C_6H_{10}O(OH)_2$. The author concludes that the hydrocarbon is as-*methylallylethylene* [*β-methyl-αδ-pentadiene*],

$CH_2{:}CH{\cdot}CH_2{\cdot}CMe{:}CH_2$. E. G.

*cyclo***Pentadiene Dibromides.** By JOHANNES THIELE (*Annalen*, 1901, **314**, 296—310. Compare Kraemer and Spilker, Abstr., 1896, i, 289; and Thiele, Abstr., 1900, i, 2).—According to the author's hypothesis, the dibromide of *cyclo*pentadiene should have the constitution of a 1 : 4-derivative,  $CH_2<\begin{array}{l}CHBr\cdot CH\\ CHBr\cdot CH\end{array}$, and not of a 1 : 2-derivative,  $CH_2<\begin{array}{l}CHBr\cdot CHBr\\ CH{=\!=}CH\end{array}$.

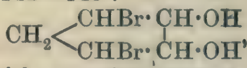
Examination of the behaviour of the hydrocarbon towards bromine has shown that two stereoisomeric 1 : 4-dibromides are formed. Each yields a dibromodihydroxy*cyclo*pentene when oxidised with potassium permanganate, chromic acid converting the glycols into αγ-dibromoglutaric acids, having to one another the relation which racemic acid bears to mesotartaric acid. The αγ-dibromoglutaric acids may be reduced to glutaric acid, showing that the hydrocarbon is a *cyclo*pentadiene, and not a methyl*cyclo*tetradiene.

*trans-cyclo*Pentadiene dibromide is the crystalline derivative described by Kraemer and Spilker (*loc. cit.*); when reduced with zinc dust and glacial acetic acid, it yields the hydrocarbon. cis-cyclo*Pentadiene dibromide*, conveniently obtained by treating the hydrocarbon with bromine dissolved in chloroform, is a colourless, refractive oil, which soon becomes turbid when exposed to light and air, liberating hydrogen bromide; it boils at 53—54° under 2 mm. pressure, and has a sp. gr. 1·9443 at 14°/4°.

trans-1 : 4-*Dibromo*-2 : 3-*dihydroxy*cyclo*pentane*,  $CH_2<\begin{array}{l}CHBr\cdot CH\cdot OH\\ CHBr\cdot CH\cdot OH\end{array}$, prepared by oxidising the *trans*-dibromide in alcohol with potassium permanganate at 0°, crystallises from benzene in small, hard prisms, and melts at 75·5°; the *di*-p-*nitrobenzoyl* derivative, $C_{19}H_{14}O_8N_2Br_2$, crystallises from toluene in yellowish needles and melts at 158—159°.

Racemic *αγ-dibromoglutaric acid*, $CH_2(CHBr{\cdot}CO_2H)_2$, obtained on oxidising the *trans*-glycol with chromic acid, crystallises in white needles or leaflets which melt and decompose at 142—143°.

cis-1 : 4-*Dibromo*-2 : 3-*dihydroxy*cyclo*pentane*,



$$CH_2{<}\begin{matrix}CHBr{\cdot}CH{\cdot}OH\\ \quad\quad\;\; | \\ CHBr{\cdot}CH{\cdot}OH\end{matrix},$$

formed when the liquid dibromide is oxidised with potassium permanganate, crystallises from benzene in small, white needles, and melts at 76—77°; the *di*-p-*nitrobenzoyl* derivative crystallises in yellowish aggregates and melts at 147—148°.

Inactive αγ-dibromoglutaric acid, obtained by oxidising the glycol with chromic acid, is identical with the product obtained by directly brominating glutaric acid. M. O. F.

Derivatives of *cyclo*Pentadiene. By JOHANNES THIELE (*Ber.*, 1901, **34**, 68—71).—*cyclo*Pentadiene, unlike indene, is very readily acted on in benzene solution by potassium, giving a *potassium* derivative which forms a yellow powder, is insoluble in benzene, inflames spontaneously in the air, is decomposed immediately by water, and reacts with halogen compounds and with carbon dioxide; the potassium derivative is not formed when the hydrocarbon is dissolved in light petroleum, or below 15°. *Bis*-cyclo*pentadienecarboxylic acid*, $(C_5H_5{\cdot}CO_2H)_2$, prepared by the action of dry carbon dioxide on the potassium derivative, crystallises from acetic acid in tablets or short prisms, melts at 210°, is only slightly soluble in hot water, is not readily acted on by sodium hydroxide or sodium amalgam, but is decomposed by heating above the melting point, and immediately decolorises alkaline permanganate. The *dimethyl* ester, $C_{14}H_{16}O_4$, crystallises from light petroleum in needles and melts at 85°, has a normal molecular weight in chloroform solution, is readily hydrolysed by alcoholic potash, and by distillation is converted into the ester of the unimolecular acid, which gradually polymerises to the crystalline bimolecular ester.

The *tetrabromide* of the dimethyl ester, $C_{14}H_{16}O_4Br_4$, separates from ethyl acetate as a white, crystalline powder, begins to decompose at 140°, and melts at about 180—185°. T. M. L.

Action of Heptylic Alcohol on its Sodium Derivative. New Method for the Synthesis of Alcohols. By MARCEL GUERBET (*Compt. rend.*, 1901, **132**, 207—210. Compare Abstr., 1899, i, 471, 472).—Heptylic alcohol, when heated at 220° in contact with its sodium derivative, undergoes a condensation similar to that effected in the case of inactive amyl alcohol. The main reaction may be thus formulated, $2C_7H_6O + C_7H_{15}ONa = C_7H_{13}O_2Na + C_{14}H_{30}O$, the products being sodium heptoate and a new alcohol derived from 2 mols. of heptylic alcohol by the elimination of 1 mol. of water.

β-Diheptylic alcohol, $C_{14}H_{29}{\cdot}OH$, is a colourless liquid with a faint odour, boiling at 151·5—152·5° under 13 mm., and at 286—289° under ordinary pressure, and having a sp. gr. 0·8405 at 15°.

A secondary reaction results from the further condensation of 2 mols. of the preceding compound with 1 mol. of sodium heptyloxide, $2C_{14}H_{30}O + C_7H_{15}ONa = C_{21}H_{44}O + C_{14}H_{27}O_2Na + 4H$. The alcoholic product, *triheptylic alcohol*, $C_{21}H_{43}OH$, a colourless, almost odourless liquid, boils at 202—206° under 13 mm. pressure, and has a sp. gr. 0·8447 at 15°. The acidic product, $C_{13}H_{27}\cdot CO_2H$, is isomeric with myristic acid and Perkin's diheptoic acid, and is termed *β-diheptoic acid*; it melts at 4°, and boils at 190—191° under 13 mm. pressure.

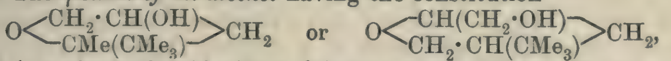
G. T. M.

Methyl*iso*propylallylcarbinol. By GEORG WAGNER, jun. (*J. Russ. Phys. Chem. Soc.*, 1900, **32**, 794—797).—*Methyl*iso*propylallylcarbinol*, $C_3H_5\cdot CMePr^{\beta}\cdot OH$, prepared by the action of zinc on a mixture of methyl*iso*propyl ketone (1 mol.) and ethyl iodide (1·5 mols.), is a colourless, mobile liquid with a faint turpentine-like odour, and is insoluble in water; it boils at 155·6° under 760 mm. pressure, and has the sp. gr. 0·85059 at 20°/0° and 0·85168 at 20°/20°. When oxidised with potassium permanganate solution, it yields the corresponding *trihydroxy*-compound, $OH\cdot CMePr^{\beta}\cdot CH_2(OH)\cdot CH_2\cdot OH$, which is a syrupy liquid, very soluble in water or alcohol, but only slightly so in ether; its *triacetyl* derivative, $C_{14}H_{24}O_6$, formed, together with a small proportion of the diacetyl derivative, when the trihydroxy-compound is heated in a sealed tube with acetic anhydride, is a viscous liquid, readily soluble in alcohol or ether, but only slightly so in water.

T. H. P.

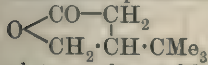
Action of Sulphuric Acid on the Trihydroxy-compound obtained by the Oxidation of Methyl*tert*butylallylcarbinol. By ALEXANDER PETCHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1900, **32**, 780—794).—By the oxidation of methyl*tert*butylallylcarbinol with potassium permanganate, a trihydric alcohol of the composition $OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot CMe(OH)\cdot CMe_3$ is obtained. The action of sulphuric acid on this alcohol gives rise to the two products:

(1) The *γ-oxide of an alcohol* having the constitution



$$O\Big<\begin{matrix}CH_2\cdot CH(OH)\\ CMe(CMe_3)\end{matrix}\Big>CH_2 \quad \text{or} \quad O\Big<\begin{matrix}CH(CH_2\cdot OH)\\ CH_2\cdot CH(CMe_3)\end{matrix}\Big>CH_2,$$

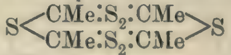
which is a viscous liquid with a faintly camphor-like smell and a cooling, caustic taste, and boils without decomposition at 214—215°; it has the sp. gr. 0·9837 at 0°/0°, 0·9699 at 20°/0°, 0·9716 at 20°/20°, 0·96998 at 20°/4°, n_D 1·45447, and its molecular refraction indicates the absence of a double linking in the molecule. The *acetyl* derivative, $C_{11}H_{20}O_2$, has been prepared and analysed. When the γ-oxide is oxidised with potassium dichromate and sulphuric acid, it yields a *γ-lactone*,

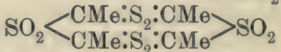


$$O\Big<\begin{matrix}CO-CH_2\\ \quad\ |\\ CH_2\cdot CH\cdot CMe_3\end{matrix}$$

, which crystallises from ether in large, quadratic plates melts at 96—98°, resolidifies at 84—82°, and dissolves readily in alcohol, but less so in water. On neutralising aqueous solutions of the lactone with baryta, lime or potassium hydroxide, *barium*, *calcium*, or *potassium* salts of an acid of the composition $C_8H_{16}O_3$ are obtained. The γ-lactone may be prepared directly by the action of sulphuric acid on β-methyl*tert*butylhydracrylic acid.

(2) An oily product which is insoluble in water, and is found to be a mixture of two ethers derived from the trihydric alcohol, one, $C_{18}H_{34}O_3$, by the removal of 3 mols. of water from 2 of the alcohol, and the other, $C_{18}H_{36}O_4$, by the removal of 2 mols. of water from 2 of the alcohol. Oxidation of the mixture with 1 per cent. aqueous potassium permanganate gives rise to the crystalline γ-lactone melting at 96—98°. T. H. P.

Ethenyltrisulphide [Tetraethenyl Hexasulphide] and its Derivatives. By Emil Fromm and Georg Mangler (*Ber.*, 1901, **34**, 204—217).—The sulphide, $C_4H_6S_3$, prepared by Bongartz (Abstr., 1886, 1000) by the action of zinc chloride on thioacetic acid, and the sulphone, $C_4H_6O_2S_3$, formed from it by oxidation, are shown by molecular weight determinations to have the double formulæ $C_8H_{12}S_6$ and $C_8H_{14}O_4S_6$; the names *tetraethenyl hexasulphide* and *tetraethenyldisulphonet etrasulphide*, and the formulæ  $\mathrm{S}\!<\!\begin{smallmatrix}\mathrm{CMe{:}S_2{:}CMe}\\ \mathrm{CMe{:}S_2{:}CMe}\end{smallmatrix}\!>\!\mathrm{S}$ and



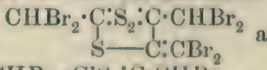
$$\mathrm{SO_2}\!<\!\begin{smallmatrix}\mathrm{CMe{:}S_2{:}CMe}\\ \mathrm{CMe{:}S_2{:}CMe}\end{smallmatrix}\!>\!\mathrm{SO_2}$$

are therefore proposed. The sulphide is stable towards alkalis, alkyl haloids, and acetic anhydride, and the disulphone is not oxidised further by chromic acid or by nitric acid.

By the action of bromine on a solution in chloroform of the hexasulphide, a *hexabromotrisulphide*, $C_6H_2Br_6S_3$, is produced, apparently by the elimination of one acetyl residue and three atoms of sulphur from the hexasulphide; it dissolves in 700 parts of boiling alcohol, crystallises on cooling in long, white, silky needles, and is readily soluble in chloroform, benzene, or carbon disulphide. Sodium methoxide or potassium hydroxide in methyl alcoholic solution converts the hexabromide into the *orthotrimethyl ester*, $C_5H_3Br_4S_3\cdot C(OMe)_3$, of a carboxylic acid; the ester forms tabular crystals, melts at 125—126°, and explodes at higher temperatures, does not lose methyl alcoholwhen heated at 82° or when boiled with chloroform or with alcohol, but is readily converted by methyl alcoholic sulphuric acid into the *monomethyl ester*, $C_5H_3Br_4S_3\cdot CO_2Me$, which crystallises from methyl alcohol, melts at 146—147°, decomposes at a slightly higher temperature, and has the normal molecular weight for the above formula. The *acid*, $C_5H_3Br_4S_3\cdot CO_2H$, crystallises from methyl alcohol or from water in long, pointed needles, begins to decompose at 130°, but when rapidly heated melts and explodes at 162°. The *ammonium* salt separates in minute needles and melts at 193—194°.

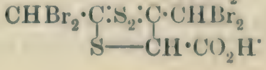
By the action of sodium ethoxide on the hexabromide, the *monoethyl ester*, $C_5H_3Br_4S_3\cdot CO_2Et$, is produced, but the orthotriethyl ester could not be obtained; the ethyl ester crystallises from alcohol in bulky aggregates of needles, melts at 115—116°, and is readily hydrolysed by alkalis to the carboxylic acid.

The formulæ suggested for the hexabromide and the carboxylic acid derived from it are



$$\begin{array}{l}\mathrm{CHBr_2\cdot C{:}S_2{:}C\cdot CHBr_2}\\ \qquad\quad\mathrm{S\text{——}C{:}CBr_2}\end{array}$$

and



$$\begin{array}{l}\mathrm{CHBr_2\cdot C{:}S_2{:}C\cdot CHBr_2}\\ \qquad\quad\mathrm{S\text{——}CH\cdot CO_2H}\end{array}$$

T. M. L.

Iodination by means of Chloride and Bromide of Iodine. By Wladimir Zernoff (*J. Russ. Phys. Chem. Soc.*, 1900, **32**, 804—819).—By the action of a mixture of iodine and bromine on glacial acetic acid in presence of red phosphorus, iodoacetic acid is formed, but no bromoacetic acid.

*a-Iodo*iso*valeric acid*, $C_5H_9O_2I$, obtained by the action of a chloroform solution of iodine monochloride (1 mol.) on a mixture of phosphorus pentachloride (1 mol.) and *iso*valeric acid (1 mol.), separates from light petroleum in nodules or from a mixture of acetone and benzene in aggregates of long, transparent prisms melting at 52°; it is readily soluble in the organic solvents but only slightly so in water, and its aqueous or alcoholic solution can be titrated with sodium hydroxide solution with phenolphthalein as indicator. The *sodium*, with aq.?, *silver*, *copper*, with $2H_2O$, *barium*, with $4H_2O$, and *zinc* salts have been prepared. On heating a sodium hydroxide solution of the iodo-acid, it is converted into α-hydroxy*iso*valeric acid, together with a small quantity of an unsaturated compound, whilst when the acid is added to boiling 15 per cent. sodium hydroxide solution, the main product is dimethylacrylic acid, the hydroxy-acid being formed only in small proportion.

a-Iodobutyric acid, $C_4H_7O_2I$, crystallises from a mixture of benzene and light petroleum in stout needles which melt at 41—42° and are readily soluble in alcohol, acetone, ether, or light petroleum, but only slightly so in water. On heating a solution of its sodium salt, the acid is converted into α-hydroxybutyric acid. T. H. P.

Simple and Mixed Acid Anhydrides. By Wilhelm Autenrieth [and, in part, J. Koburger and Paul Spiess] (*Ber.*, 1901, **34**, 168—187).—When a fatty acid is boiled for 4—6 hours with 2—3 times its weight of acetic anhydride, a mixture of the simple and mixed anhydrides of the acid is obtained; the simple anhydride is generally the principal product, and the proportion of it increases with the amount of acetic anhydride employed and with the time of heating. The mixed anhydrides do not boil as constantly as the simple anhydrides, but the extent of their decomposition during distillation is not so great as hitherto supposed; only on heating for several hours under pressure at 200—220° is the decomposition very marked, and even then it is not complete, owing to a condition of equilibrium being established.

The author has confirmed experimentally his original statement (Abstr., 1888, 250) that, when mixed anhydrides interact with phenylhydrazine, the hydrazide of the acid containing the greater amount of carbon is formed; this statement has recently been contradicted by Béhal (Abstr., 1900, i, 8), who explained the formation of *iso*valerylphenylhydrazine from acetic *iso*valeric anhydride and phenylhydrazine by assuming the latter to interact with the *iso*valeric acid formed owing to the production of acetylphenylhydrazine. It is now shown that fatty acids, contrary to Béhal's statements (*Ann. Chim. Phys.*, 1900, [vii], **19**, 284), yield at the ordinary temperature with phenylhydrazine, either alone or dissolved in ether, only salts of the base and not acylhydrazines; acetic acid yields the acetate only and *iso*valeric acid the iso*valerate* (m. p. 40—43°). The salts, moreover, do not change with time into acylhydrazines [Leighton (Abstr., 1899, i, 50) finds the reverse], and the latter are only formed by loss of water when the temperature is raised to 80—90°.

With phenols, mixed anhydrides yield nearly equal quantities of the two possible acyl derivatives, and the same is true of alcohols, although Béhal asserts that only one is formed in quantity.

The following compounds are new :—*Acetic butyric anhydride* boils at 155—175° ; with aniline (2 mols.) it yields butyranilide almost exclusively, and with phenylhydrazine, butyrylphenylhydrazine (m. p. 103° ; Schmidt, Abstr., 1889, 1159, gives 113—114°, and Vahle, Abstr., 1894, i, 411, 103°).

Acetic *iso*valeric anhydride when pure boils at 175—181°, and is more mobile than iso*valeric anhydride,* which boils at 203—208°. The former yields, with phenylhydrazine, *iso*valerylphenylhydrazine almost exclusively which melts at 110—111°, not at 101° as formerly stated ; when boiled with phenol for 2 hours, the anhydride yields phenyl acetate and *phenyl* iso*valerate,* a colourless, aromatic, heavy oil which boils at 224—226° (uncorr.). *iso*Valeric acid does not act on phenol under similar conditions.

n-*Hexoic anhydride,* $(C_6H_{11}O)_2O$, is the principal product obtained from hexoic acid and boils at 242—245° ; with warm aqueous ammonia, it yields n-*hexoamide,* which crystallises in white, nacreous leaflets and melts at 98°.

n-*Octoic anhydride* boils at 280—285°, and with phenylhydrazine yields n-*octoylphenylhydrazine,* which crystallises from alcohol in lustrous leaflets and melts at 102—104°.

With acetic anhydride, aromatic acids readily yield the simple anhydrides ; the latter are the principal products and are much more stable in contact with cold aqueous sodium carbonate than the mixed anhydrides, advantage being taken of this to effect purification. Benzoic anhydride is only dissolved by 10 per cent. aqueous sodium carbonate after boiling for ¾ hour. m-*Nitrobenzoic anhydride* crystallises from dilute alcohol in needles, melts at 47°, with ammonia yields *m*-nitrobenzamide, and with phenylhydrazine the *m*-nitrobenzoyl derivative.

m-*Bromobenzoic anhydride* was not obtained pure, but its action with ammonia and phenylhydrazine is apparently normal ; m-*bromobenzoylphenylhydrazine* crystallises from dilute alcohol in slender, colourless needles and melts at 152°.

Cinnamic acid yields an oily mixture of anhydrides which ultimately deposits crystals of cinnamic anhydride ; with ammonia, the latter yields cinnamamide (m. p. 147°, Rossum, *Zeit. Chem.*, 1866, 362, gives 141·5°), and with aniline and phenylhydrazine the corresponding anilide and phenylhydrazide. W. A. D.

Undecenoic Acid. By Hermann Thoms and Georg Fendler (*Arch. Pharm.*, 1900, **238**, 690—699).—When undecenoic acid (obtained by distilling castor oil) is oxidised by permanganate in the cold, ικ-dihydroxyundecoic acid is not the only product ; indeed, it is formed only in relatively small amount, the chief product being sebacic acid. When undecenoic acid (1 mol.) is oxidised with less than 1 mol. of permanganate at 0°, there is formed, in addition to sebacic acid, a *κ-hydroxy-ι-keto-undecoic acid*, which is soluble in benzene, melts at 90—103°, losing water meanwhile, and then has the composition $OH\cdot CH_2\cdot CO\cdot[CH_2]_8\cdot CO_2H$. The *potassium* salt of this acid and its *semicarbazone* and *acetate* (melting at 145° and 111—112° respectively) were prepared; the acid is oxidised to sebacic acid, either by mercuric oxide, bromine, or hydrogen peroxide; when it is treated with potassium cyanide and hydrochloric acid, sebacic acid is again formed. C. F. B.

Electrolysis of Hydroxy-acids: Preparation of β-Amyloxypropionic Acid and the Diamyl Derivative of Butylene Glycol. By JULES HAMONET (*Compt. rend.*, 1901, **132**, 259—261).—The alkali salts of the β-alkyloxy-acids are readily electrolysed in accordance with the equation $2OR\cdot C_nH_m\cdot CO_2K = K_2 + 2CO_2 + OR\cdot C_nH_m\cdot C_nH_m\cdot OR$, but the α-derivatives under the same conditions are to a large extent hydrolysed.

β-Amyloxypropionic acid, a colourless liquid which boils at 145—146° and at 251—252° under pressures of 15 and 750 mm. respectively, and has a sp. gr. 1·051 at 18°, is readily obtained from its *amyl* ester, a liquid boiling at 140° and 259—260° under pressures of 20 and 750 mm. respectively, and of sp. gr. 0·901 at 18°. The amyl ester is obtained by the action of sodium amyloxide in presence of amyl alcohol on *amyl β-chloropropionate*, which is obtained by the usual method, and is a colourless liquid with a fruity odour, of sp. gr. 1·024 at 18°, and boiling at 109—110° under 21 mm. pressure.

The *diamyl derivative of butylene glycol*, $C_4H_8(O\cdot C_5H_{11})_2$, an oily liquid of sp. gr. 0·849 at 18° and boiling at 260—261° under 750 mm. pressure, is obtained by the electrolysis of a solution of potassium β-amyloxypropionate with a current of about 2 amperes. C. H. B.

Wandering of Acyl Groups. By WILHELM WISLICENUS and HEINRICH KÖRBER (*Ber.*, 1901, **34**, 218).—The conversion of ethyl O-acetylacetoacetate, $CMe(OAc){:}CH\cdot CO_2Et$, into ethyl diacetoacetate, $CHAc_2\cdot CO_2Et$, takes place when the ester is heated at 200°, as well as under the influence of alkalis (Claisen and Haase, this vol., i, 118), as is shown by the production of acetylacetone. A similar change has been observed by Claisen in the case of the O-benzoate of dibenzoylmethane. T. M. L.

Complex Salts of Platinum. (IV.) Oxalonitrites of the Alkaline Earth Metals. By MAURICE VÈZES (*Bull. Soc. Chim.*, 1901, [iii], **25**, 157—165. Compare Abstr., 1898, i, 64; 1899, i, 671, 741).—*Barium platoso-oxalonitrite*, $Pt(C_2O_4)(NO_2)_2Ba,5H_2O$, is obtained by mixing cold, concentrated solutions of mol. proportions of barium chloride and potassium platoso-oxalonitrite, in the form of golden-yellow crystals having the appearance of elongated parallelograms. It becomes anhydrous at about 200°, and decomposes at about 275° with the formation of oxides of nitrogen, platinum, and barium oxalate or carbonate. It is soluble in 40 parts of cold, or 10 parts of boiling, water; the solutions decompose slowly in the cold, and more quickly on boiling, barium oxalate being precipitated.

Barium potassium platoso-oxalonitrite, $Pt_2(C_2O_4)_2(NO_2)_4BaK_2,4H_2O$, obtained in the same manner as the preceding compound, but using half the amount of barium chloride, crystallises in brownish-yellow prisms. It becomes anhydrous on heating, and finally decomposes at about 250° with the formation of oxides of nitrogen, platinum, and barium and potassium oxalates. Compounds analogous to those described are probably formed by calcium and strontium, but their instability has hitherto prevented their isolation. N. L.

Synthesis of Fumaric Acid from Glyoxylic and Malonic Acids. By Oscar Doebner (*Ber.*, 1901, **34**, 53—55).—Glyoxylic acid, which frequently occurs in plants, condenses with malonic acid in presence of pyridine at 100°, and fumaric acid results by the loss of a molecule of carbon dioxide. It is suggested that glyoxylic acid, like formaldehyde, is an important intermediate product in the formation of polybasic vegetable acids. T. M. L.

Formaldehyde as a Product of the Incomplete Combustion of Carbon Compounds. By S. P. Mulliken, J. W. Brown, and P. R. French (*Amer. Chem. J.*, 1901, **25**, 111—117. Compare this vol., ii, 43).—Loew's apparatus was employed for estimating the amount of formaldehyde produced when different carbon compounds are incompletely oxidised.

As acetaldehyde interferes with the estimation of formaldehyde, it must be removed by boiling the aqueous solution in an apparatus provided with a reflux condenser filled with water at 45—50°. Only minute traces of formaldehyde are thus lost.

Acetone gave 0·22; ethyl alcohol, 0·44; pentane, 0·88; acetic acid, 0·84; ether, 1·86; amylene, 2·01; *n*-propyl alcohol, 2·72; and trimethylcarbinol, 5·17 per cent. of formaldehyde. J. J. S.

Action of Sodium Hydroxide on *a*-Hydroxy*iso*butaldehyde. By Adolf Franke (*Monatsh.*, 1900, **21**, 1122—1132).—All the aliphatic aldehydes hitherto investigated, except formaldehyde, have given aldols under the influence of alkalis; aromatic aldehydes, on the other hand, under similar conditions, are converted quantitatively into the corresponding alcohol and acid (Cannizzaro's reaction).

a-Hydroxy*iso*butaldehyde (Abstr., 1900, i, 427) contains no hydrogen attached to the *a*-carbon atom, and therefore cannot give an aldol; it is now shown that, under the influence of warm sodium hydroxide solution, it yields *β*-methylpropyleneglycol (Wagner, Abstr., 1888, 665) and *a*-hydroxy*iso*butyric acid, and thus reacts in the same way as aromatic aldehydes. *a*-Bromo*iso*butaldehyde yields the same products when warmed with alkali. J. J. S.

Composition of a Wood Oil. By George S. Fraps (*Amer. Chem. J.*, 1901, **25**, 26—53).—The author has investigated the composition of a wood oil obtained by the distillation of hard-wood tar; after the crude product had been treated with potassium hydroxide, it was redistilled. The brownish-red oil thus obtained was carefully fractionated.

From the fractions distilling below 140°, sodium hydrogen sulphite removed methyl ethyl ketone, valeraldehyde, methyl *n*-propyl ketone, *cyclo*pentanone, and methyl *n*-butyl ketone; mesityl oxide was not present. The residues from this treatment were dried with potassium carbonate and hydrolysed with aqueous sodium hydroxide; a small quantity of ammonia was produced indicating the presence of nitriles, whilst methyl alcohol was found in the alkaline solution. The esters present were methyl acetate, propionate, *n*-butyrate, valerate, and probably α- and β-crotonates, together with small quantities of esters of organic acids of higher molecular weight than valeric acid. The oils undissolved by the sodium hydroxide were dried and fractionated; the fraction boiling below 70° yielded 2-methylfurfuran, but dimethylacetal was not present; phenylhydrazine combined with a portion of the oil, and the product yielded small quantities of diethyl and other ketones. The residue, after the removal of the esters and ketones, contained neither alcohols nor pyridines, but furnished dimethyl- and trimethyl-furfuran, together with toluene, *m*-xylene, and small quantities of unsaturated compounds.

The fractions of the oil boiling between 140° and 210° were treated with sodium hydrogen sulphite, and yielded small quantities of aldehydes and ketones. Hydrolysis with sodium hydroxide indicated the presence of methyl *n*-valerate and hexoate. Creosote was also obtained together with a small proportion of furfurans higher than trimethylfurfuran; phenol ethers were probably present in small quantities. The oils of higher boiling point, freed from ketones, aldehydes, esters, and creosote, were separated into two parts by glacial acetic acid, one soluble, the other insoluble; both absorbed bromine readily. E. G.

Density Expansion and Capillarity of Aqueous Sucrose Solutions. By J. DOMKE and H. HARTING [with F. PLATO] (*Zeit. Ver. deut. Zuckerind.*, 1900, 982—1015 and 1079—1102).—Numerous exact measurements have been made of these constants, the results being collected in tables. The following are the values of the sp. grs. of sucrose in various conditions: in solution, 1·55626 at 15°/15° and 1·5549 at 15°/4°; crystalline, 1·59103 at 15°/15° and 1·5897 at 15°/4°; crystallised (sugar candy), 1·5892 at 15°/15° and 1·5879 at 15°/4°; amorphous, 1·5090 at 15°/15° and 1·5077 at 15°/4°.

The authors find that sucrose is hygroscopic, and in air, saturated with water vapour, takes up as much as 1 per cent. of its weight of water, which it loses mostly at the ordinary temperature and completely at 90° in air of medium humidity. T. H. P.

Octabenzoylraffinose. By F. STOLLE (*Zeit. Ver. deut. Zuckerind.*, 1901, 33).—The *octabenzoyl ester of raffinose*, $C_{18}H_{25}O_{16}Bz_8$, prepared by the Schotten-Baumann method, separates from acetic acid as a crystalline powder melting at 98°. A glacial acetic acid solution containing 0·6596 gram of the ester in 50 c.c. gave a rotation of +4·1 sugar degrees in a 200 mm. tube at 18·6°. T. H. P.

Synthesis of Disaccharides. By EMIL FISCHER and E. FRANKLAND ARMSTRONG (*Sitzungsber. Akad. Wiss. Berlin*, 1901, 7, 123—131).—*Acetylchlorogalactose*, a colourless syrup produced by gently heating in sealed tubes a mixture of dry galactose and acetic chloride, decomposes on heating at 50°, reduces warm Fehling solution and is hydrolysed by water, slowly in the cold and more rapidly on warming. The substance is readily soluble in the ordinary organic solvents excepting light petroleum and in alcoholic solution undergoes decomposition with the production of hydrogen chloride and ethyl acetate; it closely resembles its analogue acetylchloroglucose (Ryan, Trans., 1899, **75**, 1055).

A disaccharide is produced by mixing together in cold alcoholic solution either of these acetylchlorohexoses with the sodium derivative of a hexose, and subsequently hydrolysing the acetyl compound first produced by the addition of cold sodium hydroxide solution; in no case has a solid product been isolated, but the aqueous solution of the condensation product has been employed in fermentation experiments and in the preparation of crystalline osazones.

Phenylgalactosidoglucosazone, a pale yellow mass of microscopic needles, melts at 155—157° corr. and dissolves in 110 parts of boiling water, crystallising from this medium and also from ethyl acetate. When produced by the action of phenylhydrazine, 50 per cent. acetic acid, and sodium chloride on a warm dilute solution of the crude disaccharide, the new compound is always mixed with the less soluble osazones of dextrose and galactose, and is separated from these by fractional crystallisation from water.

Phenylglucosidogalactosazone crystallises from benzene, toluene, or water in pale yellow needles melting at 175—177° corr.; it is somewhat less soluble than the preceding compound, requiring for solution 120 parts of boiling water.

Phenylgalactosidogalactosazone dissolves in 110 parts of hot water and crystallises in pale yellow needles melting at 176—178° corr.; it readily dissolves in alcohol, ethyl acetate, acetone, or pyridine.

Pure cultures of "bottom" yeast have no fermenting action on galactosidogalactose, but slowly destroy the other two disaccharides; the three compounds, however, are practically not affected by "top" yeast, and hence this agent serves to separate these condensation products from the monosaccharides employed in their formation.

The solutions of the disaccharides, freed in this way from hexoses, were submitted to the action of emulsin and kephir lactase; the former enzyme hydrolyses the new compounds just as it decomposes lactose and melibiose, the latter hydrolyses glucosidogalactose only, the others remaining unaffected.

Since it seems possible for enzymes to bring about the formation of disaccharides from hexoses (Hill, Trans., 1898, **73**, 634) a mixture of galactose and dextrose was treated with an extract of kephir ferment, and after remaining for three months at 30° yielded an osazone readily soluble in water or toluene, crystallising in yellow needles, melting at 193—196° corr. and closely resembling phenyllactosazone.

G. T. M.

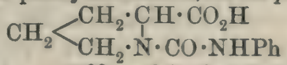
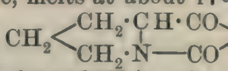
Amino-acids. By HANS MEYER (*Monatsh.*, 1900, **21**, 913—948).—The acidity of an amino-acid depends on the electrochemical character of the groups near to the amino-nitrogen atom; when this, or the carbon atom to which it is linked, is united to positive groups, the amino-acid has a neutral or only faintly acid reaction, as, for example, in the primary and alkyl-substituted aliphatic amino-acids, piperidinecarboxylic and pyrrolidinecarboxylic acids and betaines; when it is united to negative groups, the amino-acid reacts as a true acid, for example, in such compounds as methyleneglutamine, aromatic aminocarboxylic acids and pyridinecarboxylic and quinolinecarboxylic acids. Substitution of an amino-hydrogen atom by alkyl in an aromatic amino-acid slightly decreases the acid reaction. The stability of the esters is, as a rule, the opposite of that of the acids—a stable acid, such as glycine, forming a very unstable ester; those acids in which the basic function of the amino-group is neutralised by the presence of a negative group are stable and form stable esters, whilst those in which the α-carbon atom is united to strongly negative groups are unstable, but form stable esters. All acid imides are hydrolysed by one equivalent of an alkali to the neutral salt of an amino-acid.

The following alkyl-substituted anthranilic acids were prepared by the action of the alkyl iodides on an aqueous solution of potassium anthranilate: *ethylanthranilic acid*, which crystallises in colourless, long needles and melts at 152—153°; n-*propylanthranilic acid*, which crystallises in greenish, flat needles and melts at 110°; iso*butylanthranilic acid*, which crystallises in colourless, long needles and melts at 84°; iso*amylanthranilic acid*, which crystallises in colourless, long needles and melts at 68—70°. R. H. P.

Glycine. By ADOLF JOLLES (*Zeit. physiol. Chem.*, 1900, **31**, 389—394. Compare this vol., i, 30).—When glycine is boiled with potassium hydroxide solution for several hours, only small quantities of ammonia and acetic acid are formed. Glycine reacts with sodium hypobromite, although little or no nitrogen is evolved; that a complex change has taken place is proved by the fact that the whole of the nitrogen is found in the precipitate obtained with phosphotungstic acid, whereas glycine itself yields no precipitate with this reagent. The nitrogen in the precipitate is mainly liberated as ammonia on boiling with concentrated potash, and formic acid is obtained when the alkaline residue is acidified and distilled. J. J. S.

Synthesis of $\alpha\delta$-Diaminovaleric Acid. By EMIL FISCHER (*Sitzungsber. Akad. Wiss. Berlin*, 1900, **52**, 1111—1121; *Ber.*, 1901, **34** 454—464).—*Ethyl γ-phthaliminopropylbromomalonate,*

$$C_8H_4O_2N\cdot[CH_2]_3\cdot CBr(CO_2Et)_2,$$

obtained by the action of bromine on diethyl γ-phthaliminopropylmalonate, crystallises in prisms or plates, melts at 51° (corr.), and is decomposed in the cold by alkalis; when treated with ammonia, and then with hydrochloric acid, it yields phthalic acid and α-pyrrolidinecarboxylic acid, which, when treated with phenylcarbimide, forms *phenylcarbimino-2-pyrrolidinecarboxylic acid,*  $CH_2<\begin{matrix}CH_2\cdot CH\cdot CO_2H\\ |\\ CH_2\cdot N\cdot CO\cdot NHPh\end{matrix}$; this crystallises from acetone, melts at about 170°, and is then converted into the inner *anhydride,*  $CH_2<\begin{matrix}CH_2\cdot CH\cdot CO\\ |\\ CH_2\cdot N—CO\end{matrix}>NPh$, which crystallises in colourless prisms and melts at 118° (corr.). *γ-Phthaliminopropylbromomalonic acid,* obtained from the ester by hydrolysis with hydrogen bromide, crystallises with $2H_2O$, and decomposes at about 140—145° with the formation of *δ-phthalimino-α-bromovaleric acid,* $C_8H_4O_2N\cdot[CH_2]_3\cdot CHBr\cdot CO_2H$, which crystallises from benzene, melts at 127—128° (corr.), and when treated successively with ammonia and hydrochloric acid is converted into *αδ-diaminovaleric acid.*

The dibenzoyl derivative of αδ-diaminovaleric acid is identical with ornithuric acid, and can be partially hydrolysed to the monobenzoyl derivative, which is identical with that obtained by Jaffé (Abstr., 1878, 585) from ornithuric acid. *αδ-Diaminovaleric acid* is probably the optically inactive form of ornithin. R. H. P.

Esters of Amino-acids. By Emil Fischer (*Sitzungsber. Akad. Wiss. Berlin*, 1900, **48**, 1062—1083; *Ber.*, 1901, **34**, 433—454).—The esters of the amino-acids are best prepared from the hydrochlorides by treatment with concentrated aqueous alkalis, hydrolysis is avoided at a low temperature, and when the solution has been saturated with potassium carbonate, the esters can be completely extracted with ether. With the exception of the crystalline derivatives of tyrosine, these esters are liquids, which have an alkaline reaction and can be distilled under reduced pressure; the solubility in water decreases with increasing molecular weight, the derivatives of aspartic and glutamic acids being, however, very soluble; the boiling points often lie wide apart, and the esters can be separated by fractional distillation, thus the isolation of the amino-acids from complicated mixtures, such as are obtained, for instance, by the hydrolytic decomposition of proteids, can be effected by the fractional distillation of the esters; they are easily hydrolysed by boiling with water or barium hydroxide, are characterised by their picrates, and easily form derivatives when treated with acid anhydrides, acid chlorides, halogen alkyls, carbimides, thiocarbimides, aldehydes, ketones, or carbonyl chloride; when heated with alcohol they are converted into compounds analogous to glycine anhydride.

The ethyl ester of glycine forms a *picrate* which crystallises in quadratic prisms and melts at 157° (corr.); it condenses with ethyl acetoacetate to form *diethyl acetoaceticglycine*, $CO_2Et\cdot CH\colon CMe\cdot NH\cdot CH_2\cdot CO_2Et$, which crystallises in clusters of colourless, long needles and melts at 53°, with acetylacetone to form *ethyl acetylacetoneglycine*,

$$CHAc\colon CMe\cdot NH\cdot CH_2\cdot CO_2Et,$$

which is obtained as a crystalline mass melting at 68° (corr.), with acetonylacetone to form a yellow oil, which turns a pine splinter, moistened with hydrochloric acid, a deep red colour, and when treated with alkalis yields 2:5-*dimethylpyrrole*-1-*acetic acid*, which crystallises in needles, melts at 130—131°, and decomposes in contact with moist air. Glycine ethyl ester, when treated with phenylthiocarbimide, yields *ethyl phenylthiocarbiminoacetate*, $NHPh\cdot CS\cdot NH\cdot CH_2\cdot CO_2Et$, which crystallises in rhombic plates, melts at 85°, and gives a red solution with alkalis; when treated with phosgene, it yields *diethyl carbamidodiacetate*, $CO(NH\cdot CH_2\cdot CO_2Et)_2$, which crystallises in long, slender prisms and melts at 146° (corr.).

Alanine ethyl ester boils at 48° under 11 mm. pressure, has a sp. gr. 0·9846 at 12·5°, and forms a *picrate* which crystallises in yellow needles, and melts at 171° (corr.); when kept for some weeks, it is converted into the corresponding lactimide (3:6-dimethyl-2:5-diketopiperazine).

The *hydrochloride* of ethyl α-aminobutyrate, obtained by passing hydrogen chloride into an alcoholic solution of α-aminobutyric acid, crystallises in needles, and can be readily converted into the free *ester*, which boils at 61·5° under 11 mm. pressure, has a sp. gr. 0·9655 at 12·5°, and forms a *picrate* which crystallises in slender prisms and melts at 127° (corr.); *ethyl β-aminobutyrate* boils at 59—60° under 12·5 mm. pressure; attempts to esterify γ-aminobutyric acid resulted in the formation of its anhydride, the pyrrolidone, which boiled at 153° under 12 mm. pressure; 3 : 6-*diethyl*-2 : 5-*diketopiperazine*, $C_4H_4O_2N_2Et_2$, obtained by heating ethyl α-aminobutyrate at 170°, crystallises in lustrous leaflets and melts at 265° (corr.).

i-*Ethyl leucine* boils at 83·5° under 12 mm. pressure, has a sp. gr. 0·929 at 17°, forms a *picrate* which crystallises in yellow needles and melts at 136° (corr.), and a d-*tartrate*, which crystallises in lustrous leaflets and melts at 145° (corr.); the l-*ethyl* ester has a rotation $[\alpha]_D$ +13·1° at 20°, is not racemised when hydrolysed, and forms a *picrate* which crystallises in small needles and melts at 129·5° (corr.). By means of this ester, pure *l*-leucine can be isolated from the products of the hydrolysis of horn; *leucinimide* (3 : 6-*diïsobutyl*-2 : 5-*diketopiperazine*) crystallises from alcohol and melts at 271° (corr.); the *benzenesulphonic* derivative of *d*-leucine crystallises in clusters of needles, melts at 119—120° (corr.), and has $[\alpha]_D$ −39° at 20° (compare Abstr., 1900, i, 647), i-*acetyl leucine* crystallises in needles and melts at 161° (corr.).

i-*Ethyl α-amino*-n-*caproate* boils at 90—91° under 11 mm. pressure, has a sp. gr. 0·9335 at 17°, forms a *picrate* which crystallises in prisms melting at 124° (corr.), and, when heated, yields 3 : 6-*dibutyl*-2 : 5-*diketopiperazine*, which crystallises in lustrous leaflets and melts at 268° (corr.). i-*Phenyl-α-alanine ethyl ester* is a viscous oil which has a sp. gr. 1·065 at 15°, and boils at 143° under 20 mm. pressure; it forms a *picrate* which crystallises in flat prisms melting at 156·5° (corr.), and when heated at 180° for 24 hours yields the phenyllactimide.

l-*Tyrosine ethyl ester* crystallises in flat prisms, melts at 108—109° (corr.) has $[\alpha]_D$ +20·4° at 20°, and, when heated at 180° for 24 hours is converted into a piperazine derivative. *Sarcosine ethyl ether* boils at 43° under 10 mm. pressure, has a sp. gr. 0·971 at 15·5°, and forms a *picrate* which crystallises in needles and melts at 149° (corr.). l-*Diethyl aspartate* is a viscous oil which boils at 126·5° under 11 mm. pressure, has a sp. gr. 1·089 at 17° and $[\alpha]_D$ −9·46° at 20°. d-*Diethyl glutamate* boils at 139—140° under 10 mm. pressure, has a sp. gr. 1·0737 at 17° and $[\alpha]_D$ +7·34° at 20°.

R. H. P.

Canarin and ψ-Thiocyanogen. By ALWIN GOLDBERG (*J. pr. Chem.*, 1901, [ii], 63, 41—48).—Canarin obtained from thiocyanates, and the ψ-thiocyanogen products prepared by various chemical methods, are quite distinct substances. The author has determined the quantity of each produced from potassium thiocyanate by treatment with chlorine, bromine, fuming nitric acid, or potassium chlorate and hydrochloric acid, and from ammonium thiocyanate by interaction with ammonium persulphate.

Canarin is separated from the ψ-thiocyanogen products as the slightly soluble sodium salt; on the addition of hydrochloric acid to a solution of this salt, canarin, $(C_8H_6ON_8S_7)_x$, is obtained as a light brown precipitate which, when dry, forms a yellowish-red powder. It is extremely stable towards reducing agents; of its decomposition products obtained under various circumstances, cyanuric acid and its derivatives may be mentioned. In the formation of alkali salts, one-third of its hydrogen is replaced by the alkali metals.

By the action of a dry halogen on a dry thiocyanate, and the treatment of the resulting thiocyanogen, $(CNS)_x$, with alkali hydroxide, canarin is obtained in a yield of 30—40 per cent. of the thiocyanate employed. After the separation of the canarin sodium derivative, the residual alkaline solution yields, on addition of hydrochloric acid, a yellow, amorphous *substance*, $C_3H_4ON_4S_2$, in a quantity of about one-third to one-half of the dye produced in the same reaction; the filtrate contains sulphuric acid, hydrocyanic acid, and ammonia. When the substance, $C_3H_4ON_4S_2$, is heated with hydrochloric acid under pressure, it yields cyanuric acid; on treatment with ammonium sulphide under pressure, it furnishes dithiomelanurenic acid, and with ammonia under pressure, thioammeline. E. G.

Preparation of Doubly Unsaturated Hydrocarbons. By Carl Harries (*Ber.*, 1901, **34**, 300—304).—When the phosphates of certain diamines are distilled, ammonia, ammonium pyrophosphate and an unsaturated hydrocarbon containing two double bonds are formed. The hydrochloride and sulphate of the diamine are less suited for this purpose.

[With Suren Adamiantz].—*Diacetoneaminoxime*,

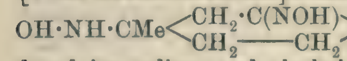
$$NH_2\cdot CMe_2\cdot CH_2\cdot CMe\colon NOH,$$

is obtained from diacetonamine, hydroxylamine hydrochloride, and potassium carbonate (compare Abstr., 1896, i, 318); it melts at 55—56°, and boils at 129—131° under 14 mm. pressure. It is reduced by sodium and alcohol to *βδ-diamino-β-methylpentane*,

$$NH_2\cdot CMe_2\cdot CH_2\cdot CHMe\cdot NH_2;$$

this boils at 36—41° under about 12 mm. pressure, and forms a *phosphate* which melts at 187—188°. When the phosphate is distilled, *methylisoprene* (*methylpentadiene*), C_6H_{10}, perhaps $C_2H\colon CMe\cdot CH\colon CHMe$, is formed; it boils at 75—77° under 779 mm. pressure, and has sp. gr. 0·71761 at 16°.

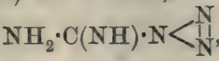
[With Ernest Atkinson].—Methyl*cyclo*hexenonehydroxylamino-oxime,

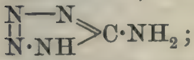


$$OH\cdot NH\cdot CMe<\begin{matrix}CH_2\cdot C(NOH)\\ CH_2\text{——}CH_2\end{matrix}>CH_2,H_2O$$

(Abstr., 1898, i, 402), is reduced by sodium and alcohol to a *diamine*, $C_7H_{16}N_2$, which boils at 85—89° under 17 mm. pressure, and forms a *sulphate*, with $H_2SO_4.2H_2O$, which was analysed. When the phosphate of the diamine is distilled, a *dihydrotoluene* (*methyl*cyclo*hexadiene*), C_7H_{10}, is obtained; this boils at 107—108° under 779 mm. pressure. C. F. B.

Hydrouracil. By Julius Tafel (*Ber.*, 1901, **34**, 144).—The substance recently described by the author and Weinschenk (this vol., i, 72) as hydrouracil has been previously described by Weidel and Roithner (Abstr., 1896, i, 470) as β lactylcarbamide. A. H.

So-called Diazoguanidine. By Arthur Hantzsch and A. Vagt (*Annalen*, 1901, **314**, 339—369).—In many respects, the behaviour of diazoguanidine (Thiele, Abstr., 1892, 1298) is inconsistent with that of a true diazo-compound. The authors' investigation shows that the salts of diazoguanidine, originally represented by the formula $NH_2{\cdot}C(NH){\cdot}NH{\cdot}N{:}N{\cdot}X$, are actually derivatives of *carbaminoimino-azoimide*,  $NH_2{\cdot}C(NH){\cdot}N{<}\begin{matrix}N\\ \|\\ N\end{matrix}$, and brings out the analogy between this compound and carbaminoazoimide (Thiele and Stange, Abstr., 1895, i, 252).

Carbaminoiminoazoimide nitrate is acid towards litmus, the aqueous solution, when boiled, yielding nitric acid and aminotetrazole,  $\begin{matrix}N{-}N\\ \|\quad\\ N{\cdot}NH\end{matrix}{>}C{\cdot}NH_2$; the *nitrate* of the last-named substance crystallises from alcohol and melts at 174—175°, when it decomposes. Carbaminoiminoazoimide *hydrogen sulphate*, obtained by adding concentrated sulphuric acid to an alcoholic solution of the nitrate, behaves in a similar manner, yielding aminotetrazole and sulphuric acid; when heated with dilute sulphuric acid, the same change is brought about, 20 per cent. of azoimide also being produced. When the nitrate is reduced with cold stannous chloride, nitrogen is the main product, whilst hydrogen sulphide gives rise to nitrogen and guanidine.

Carbaminoazocyanide (*aminohydroxymethylcyanotriazen*),

$$NH_2{\cdot}CO{\cdot}NH{\cdot}N{:}N{\cdot}CN,$$

obtained from carbaminoazoimide and hydrogen cyanide, is a brownish-yellow powder which darkens at 250°, and decomposes completely at higher temperatures; it is insoluble in water and all organic solvents, but forms alkali derivatives from which it may be regenerated by dilute acids.

Thiele observed that carbaminoiminoazoimide nitrate is resolved by sodium hydroxide (2 mols.) into cyanamideazoimide. The authors have succeeded in showing that carbaminoiminoazoimide is first formed from the action of the alkali (1 mol.); it exists unquestionably in the aqueous solution, but on evaporating the liquid, aminotetrazole is produced. When a cold aqueous solution of carbaminoiminoazoimide is treated with sodium hydroxide (2 mols.), cyanic acid and azoimide are produced, and conversely, carbaminoiminoazoimide may be synthesised from the two substances last named; similarly, aminotetrazole, which sodium hydroxide converts into cyanamide and azoimide, is produced when these compounds are brought together.

as-*Dibenzylcyanamide*, $CN{\cdot}N(CH_2Ph)_2$, prepared from cyanamide and benzyl iodide at 50°, crystallises from ether in lustrous, white leaflets, and melts at 53—54°; it is identical with Wallach's cyanodibenzylamine (Abstr., 1899, i, 659). M. O. F.

Remarks on the Relation of Inorganic to Organic Chemistry. By August Michaelis (*Annalen*, 1901, **314**, 276—280).—The author discusses the development and future of that branch of chemistry which deals with organic compounds containing such elements as phosphorus, arsenic, boron, silicon, sulphur, selenium, and tellurium.

M. O. F.

Direct Hydrogenations Effected in the Presence of Reduced Nickel: Preparation of Hexahydrobenzene. By Paul Sabatier and Jean B. Senderens (*Compt. rend.*, 1901, **132**, 210—212. Compare Abstr., 1897, i, 305, 545; 1899, i, 555).—When hydrogen, saturated at the ordinary temperature with the vapour of benzene, is led over finely divided nickel at 180—200°, combination of the two gaseous reagents takes place, resulting in the formation of *cyclo*hexane. The liquid product is quite free from benzene and its partially hydrogenated derivatives. When the hydrocarbon is in excess the product consists of *cyclo*hexane and unaltered benzene. At 300°, the *cyclo*hexane is decomposed while still in contact with the nickel, and yields methane and a deposit of carbon. In all probability, the first stage of this reaction consists in the decomposition of 1 mol. of the *cyclo*hexane into 3 mols. of ethylene, the gaseous hydrocarbon being then broken up into methane and carbon (compare Abstr., 1897, i, 305, 545). The higher homologues of benzene also undergo hydrogenation in a similar manner, whilst nitrobenzene is easily reduced to aniline.

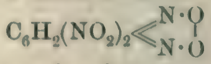
G. T. M.

Constitution of Benzene. By George M. Richardson (*Amer. Chem. J.*, 1901, **25**, 123—144).—The author draws attention to a number of properties in which ortho- and para-derivatives of benzene resemble one another, but in which they differ from isomeric meta-compounds. Among the points dealt with are (1) Phenomena of substitution; (2) influence of substituents on the properties of a compound; (3) phenomena of reduction and oxidation. The conclusion drawn is that Claus' diagonal formula best represents the structure of the benzene molecule.

J. J. S.

Formation and Preparation of Propylbenzene. By F. Bodroux (*Compt. rend.*, 1901, **132**, 155—157).—The hydrocarbons, $\alpha\gamma$-diphenylpropane, and propylbenzene, are produced by heating at 60° a mixture of benzene, aluminium chloride, and trimethylene dibromide. The propylbenzene, on treatment with bromine and aluminium bromide, yields pentabromopropylbenzene and a small quantity of hexabromobenzene; the latter substance is produced from *iso*propylbenzene, and the quantity obtained shows that the crude hydrocarbon consists chiefly of *n*-propylbenzene with 1·3 per cent. of cumene. The hydrocarbon produced from benzene and propylene dibromide in the presence of aluminium chloride consists almost wholly of the normal isomeride, only a trace of hexabromobenzene being obtained on bromination. The hydrocarbon derived from $\alpha\beta$-diphenylpropane by distilling this substance from powdered aluminium chloride yields equivalent proportions of pentabromopropylbenzene and hexabromobenzene, and therefore consists of equal quantities of *n*-propylbenzene and cumene.

G. T. M.

Tetranitrobenzene, Nitrodinitrosobenzene, and Trinitrophenylhydroxylamine. By Rudolf Nietzki and Richard Dietschy (*Ber.*, 1901, **34**, 55—60).—By the action of picryl chloride on hydroxylamine hydrochloride in presence of sodium acetate, a *dinitrodinitrosobenzene* is produced, to which the formula  $C_6H_2(NO_2)_2<\begin{array}{l}N\cdot O\\ \quad\;\,|\\ N\cdot O\end{array}$ $[(NO_2)_2:(NO)_2=1:3:4:5]$ is assigned; it separates in glistening, golden flakes, melts at 133°, dissolves readily in hot water, alcohol, ether, or acetic acid, and is perhaps the same substance which Michael and Brown (Abstr., 1887, 663) described as dipicrylhydroxylamine. Like dinitrosobenzene, it is relatively very stable, but is oxidised by nitric acid of sp. gr. 1·52 to 1 : 2 : 3 : 5-*tetranitrobenzene*, $C_6H_2(NO_2)_4$, which crystallises from alcohol in minute, yellow needles, melts at 116°, is reduced by stannous chloride and hydrochloric acid to tetraminobenzene, and with *aniline* forms an additive product crystallising from alcohol in red needles and melting at 180°.

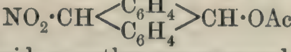
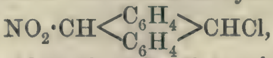
2 : 4 : 6-*Trinitrophenyl*-1-*hydroxylamine*, $C_6H_2(NO_2)_3\cdot NH\cdot OH$, formed by the action of picryl chloride on hydroxylamine hydrochloride when no sodium acetate is used, crystallises from alcohol, in which it is only slightly soluble, in minute, yellow needles, melts at 174°, and differs entirely from the substance melting at 99—100° which Michael and Brown prepared by the action of hydroxylamine on ethyl picrate, and described as picrylhydroxylamine; it forms an additive product with aniline, is reduced by stannous chloride and hydrochloric acid to tetraminobenzene, and by ammonium sulphide to dinitrodiaminobenzene, and is oxidised by nitric acid to tetranitrobenzene. Alcoholic potassium hydroxide converts the hydroxylamine into iso*picric acid*, $C_6H_3O_7N_3$, which crystallises from water or alcohol in dark yellow needles and melts at 117—118° (picric acid melts at 122°); the *potassium* salt crystallises in brown flakes with a violet lustre, and is three times as soluble in water as potassium picrate; the structure of the acid has not been determined, but it is suggested that one of the nitro-groups has been replaced by hydroxyl, and the hydroxylamine group oxidised to a nitro-group.

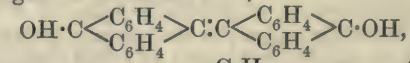
1 : 3 : 5-*Trinitro*-2-*nitrosobenzene*, $C_6H_2(NO_2)_3\cdot NO$, prepared by oxidising the hydroxylamine with chromic acid in acetic acid solution, crystallises from acetic acid in greenish-yellow flakes, melts at 198°, and shows a normal molecular weight when dissolved in boiling benzene. Nitric acid of sp. gr. 1·52 does not oxidise it to tetranitrobenzene, but converts it into a substance, $C_6H_3O_6N_3$, having the composition of a trinitrobenzene, but which is regarded as 3 : 5-*dinitro*-4-*nitrosophenol*, $NO\cdot C_6H_2(NO_2)\cdot OH$, or 3 : 5-*dinitroquinone*-4-*monoxime*,

$$O\colon C_6H_2(NO_2)_2\colon NOH;$$

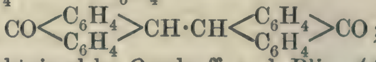
it crystallises from alcohol in yellow needles, melts at 110°, dissolves in alkali carbonates, and is reprecipitated by acids. T. M. L.

Action of Nitric Acid on Anthracene. By Otto Dimroth (*Ber.*, 1901, **34**, 219—223. Compare Meisenheimer, this vol., i, 135). —Nitroanthracene can be obtained, not only from the products, $C_{14}H_{10},HNO_3$ and $C_{14}H_{10},2NO_2$, obtained by Liebermann and Lindemann by the action of nitrous fumes on anthracene (Abstr., 1881, 99), and the compound, $C_{14}H_{10},EtNO_3$, prepared by the action of nitric acid and alcohol on anthracene (A. G. Perkin, Trans., 1891, **59**, 637), but also by the action of alkalis on the nitroacetate and nitrochloride.

Anthracene nitroacetate,  $NO_2\cdot CH{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}CH\cdot OAc$, prepared by the action of 1 mol. of nitric acid on anthracene suspended in glacial acetic acid, is a yellow substance which has not been crystallised, but is converted by warm dilute sodium hydroxide into nitroanthracene. The *nitrochloride*,  $NO_2\cdot CH<\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}>CHCl$, prepared by adding strong hydrochloric acid to the nitration mixture, crystallises from benzene in broad, colourless needles, melts at about 163°, and is readily converted into nitroanthracene, the yield of which exceeds slightly the weight of anthracene used. Nitroanthracene is also produced when sulphuric acid is added to the nitration mixture, but without this addition the mixture slowly decomposes, giving, at first, a *substance* which separates in stout, white crystals, dissolves in dilute sodium hydroxide with an intense red coloration, crystallises from benzene in white needles, and melts at 135°; anthraquinone subsequently separates. When heated on the water-bath, a substance, $C_{28}H_{18}O_2$, is produced which is regarded as *dianthranol*,

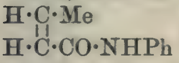
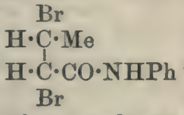


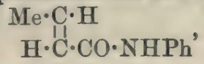
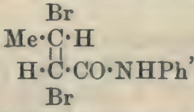
$$OH\cdot C<\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}>C:C<\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}>C\cdot OH,$$

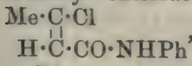
or, more probably, *dianthrone*,  $CO<\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}>CH\cdot CH<\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}>CO$; this is identical with the product obtained by Orndorff and Bliss (Abstr., 1896, i, 570) from anthranol, and described by them as a polymeride, $C_{28}H_{20}O_2$; the fact that it is an oxidation product is shown by its formation from anthranol by treatment with ferric chloride, a reaction analogous to the formation of α- and β-dinaphthols from α- and β-naphthols. T. M. L.

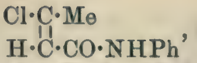
Triphenylchloromethane. By JAMES F. NORRIS and WARREN W. SANDERS (*Amer. Chem. J.*, 1901, **25**, 54—62. Compare Gomberg, Abstr., 1901, i, 77).—The authors have obtained a nearly theoretical yield of triphenylchloromethane by a method differing somewhat from that recently described by Gomberg; they have also isolated a brown, crystalline intermediate *product*, $Al_2Cl_6,2CPh_3Cl$, which decomposes rapidly in the air, and when heated begins to decompose at 122—125°. E. G.

Non-existence of Tervalent Carbon. By JAMES F. NORRIS (*Amer. Chem. J.*, 1901, **25**, 117—122. Compare Gomberg, this vol., i, 77).—The reaction of zinc on triphenylchloromethane is much more rapid in ethyl acetate then in benzene solution; in the former case, hydrogen is evolved and the action completed within 2—3 minutes, whereas in benzene solution the action goes on for 5—6 days and no hydrogen is evolved. The product obtained by either method when brought into contact with air yields Gomberg's peroxide. The authors conclude that Gomberg's unsaturated hydrocarbon, triphenylmethyl (*loc. cit.*), is really *diphenylphenylenemethane*, $CPh_2:C_6H_4$, and is obtained by the elimination of hydrogen chloride from the chloro-derivative. Gomberg's peroxide is only formed when moist air acts on the hydrocarbon, and is hence probably due to the combined action of moisture and oxygen. The action of iodine on the hydrocarbon, if the author's view of its constitution be accepted, must be due to the intermediate formation of hydrogen iodide. In many properties, diphenylphenylenemethane resembles tetrahydronaphthalene. J. J. S.

Crotonic and *iso*Crotonic Acids. By WILHELM AUTENRIETH and PAUL SPIESS (*Ber.*, 1901, **34**, 189—197).—On boiling crotonic acid with acetic anhydride, a mixture of acetic crotonic anhydride and crotonic anhydride is apparently obtained (compare this vol., i, 185), which, without further purification, yields with aniline the *anilide*  $\begin{array}{l}\mathrm{H\cdot C\cdot Me}\\ \;\;\|\\ \mathrm{H\cdot C\cdot CO\cdot NHPh}\end{array}$; this crystallises from water in colourless, lustrous needles or thick prisms, melts at 115°, dissolves in 2000 parts of water at 15°, and can also be obtained by the action of aniline on crotonyl chloride, formed by the action of phosphorus pentachloride on crotonic acid. With bromine, the anilide yields *aβ-dibromobutyryl-anilide*,  $\begin{array}{l}\quad\mathrm{Br}\\ \mathrm{H\cdot C\cdot Me}\\ \;\;|\\ \mathrm{H\cdot C\cdot CO\cdot NHPh}\\ \quad\mathrm{Br}\end{array}$, which crystallises from dilute alcohol in lustrous plates, melts at 159°, and is also formed from Kolbe's *aβ*-dibromobutyric acid (*J. pr. Chem.*, 1842, **25**, 385) by the successive action of phosphorus pentachloride and aniline.

iso*Crotonylanilide*,  $\begin{array}{l}\mathrm{Me\cdot C\cdot H}\\ \;\;\;\;\|\\ \mathrm{H\cdot C\cdot CO\cdot NHPh}\end{array}$, is formed by the action of aniline on the mixed anhydrides obtained by boiling acetic anhydride with *iso*crotonic acid; it crystallises from water at 60° in slender, silky needles, melts at 73—74°, and is soluble in 1100 parts of water at the ordinary temperature. When *iso*crotonic acid is treated with phosphorus pentachloride at the ordinary temperature, and then with aniline, it yields, not *iso*crotonylanilide, but the isomeric crotonylanilide, owing to the *iso*crotonyl chloride being transformed into crotonyl chloride; if, however, during the formation of the chloride, the mixture is cooled, no such change occurs, and *iso*crotonylanilide is ultimately obtained. The latter is completely transformed into crotonylanilide when heated for 8 hours at 180—200°, and is thus the labile form of the anilide. iso-*aβ-Dibromobutyrylanilide*,  $\begin{array}{l}\quad\;\;\mathrm{Br}\\ \mathrm{Me\cdot C\cdot H}\\ \;\;\;\;\|\\ \mathrm{H\cdot C\cdot CO\cdot NHPh}\\ \quad\;\;\mathrm{Br}\end{array}$, obtained from it by the addition of bromine, melts at 115°, and is more soluble in alcohol than its isomeride; it is also formed by the successive treatment of *iso-aβ*-dibromobutyric acid with phosphorus pentachloride and aniline. These facts establish the correctness of Wislicenus' views (Abstr., 1889, 236) as to the existence of two different dibromobutyric acids.

With acetic anhydride, both *β*-chlorocrotonic acid and *β*-chloro*iso*crotonic acid yield the corresponding anhydrides, which interact normally with aniline and phenylhydrazine; it is noteworthy that the former acid is not converted by this treatment into the *iso*-acid, although rapidly transformed by phosphorus pentachloride into *iso*crotonyl chloride (Abstr., 1896, i, 591). *β-Chloro*iso*crotonylanilide*,  $\begin{array}{l}\mathrm{Me\cdot C\cdot Cl}\\ \;\;\;\;\|\\ \mathrm{H\cdot C\cdot CO\cdot NHPh}\end{array}$, crystallises from dilute alcohol in slender prisms melting at 108°, and the *phenylhydrazide* from benzene on adding light petroleum in lustrous leaflets melting at 114°. *β-Chlorocrotonyl-*

anilide,  $\begin{matrix}Cl\cdot C\cdot Me\\ \| \\ H\cdot C\cdot CO\cdot NHPh\end{matrix}$, forms slender needles melting at 122—123°, and the *phenylhydrazide* flat needles melting at 130°. W. A. D.

Synthesis of Amines by the Aid of Alkyl Salicylates. By ALFRED TINGLE (*Amer. Chem. J.*, 1901, **25**, 144—155. Compare Abstr., 1900, i, 544 and 641).—It has previously been shown that secondary amines are obtained by the action of alkyl salicylates on aniline. Ammonia acts on methyl salicylate at its boiling point, yielding dimethylaniline and salicylamide, the latter being then partly converted into polysalicylonitrile; the reaction between ammonia and ethyl or *iso*amyl salicylate is so slow that the products could not be investigated. Benzanilide is the only product obtained by the action of aniline on methyl benzoate, whether the former is in excess or not. Benzoic acid and dimethylaniline give a small amount of methyl benzoate and a tarry substance. It is probable that the action between an aromatic ester and aniline is a reversible one, $R\cdot CO_2R' + NH_2Ph \rightleftarrows R\cdot CO_2H + NHPhR'$, but that in the case of salicylates the reaction becomes no longer reversible owing to the fact that the salicylic acid is decomposed into phenol and carbon dioxide as fast as it is formed.

When methyl salicylate (2 mols.) and aniline (1 mol.) are boiled for 6 hours, the product is dimethylaniline, and not methylaniline, the product formed when aniline is in excess.

Methyl *p*-hydroxybenzoate (1 mol.) and aniline (3 mols.), when boiled for 4 hours, give dimethylaniline and phenol in addition to the unchanged substances. *Methyl* m-*hydroxybenzoate* crystallises from a mixture of benzene and light petroleum in colourless needles melting at 70°. When boiled with excess of aniline, it is partly converted into *m*-hydroxybenzanilide, but no secondary or tertiary base is formed, no doubt owing to the fact that the acid, unlike the ortho- and para-acids, is stable. J. J. S.

Dimethylaniline Oxide. By EUGEN BAMBERGER and PAUL LEYDEN (*Ber.*, 1901, **34**, 12—26. Compare Bamberger and Tschirner, Abstr., 1899, i, 347 and 682).—In preparing dimethylaniline oxide, the yield is improved by using hydrogen peroxide previously neutralised with magnesia. Small quantities of nitrobenzene are formed, apparently owing to the following changes, $NPhMe_2 \rightarrow NHPhMe \rightarrow PhNO \rightarrow Ph\cdot NO_2$.

When dry dimethylaniline oxide hydrochloride is heated in a stream of carbon dioxide for 150 hours at 75—80°, it yields 26 per cent. of its weight of a mixture of dimethylaniline and methylaniline in the proportion 3 : 2, along with traces of aniline and *o*-dimethylaminophenol, 6 per cent. of a mixture of tetramethyl-*pp*-diaminodiphenylmethane, $CH_2(C_6H\cdot NMe_2)_2$, and bisdimethylaniline (Lippmann and Lange, Abstr., 1881, 161), and about 8 per cent. of mixed *p*-dimethylaminophenol (von Pechmann, *Ber.*, 1899, **32**, 3682, note) and *p*-aminophenol; 18 per cent. of a violet amorphous powder is also formed along with 10 per cent. of resin and about 2 per cent. of a crystalline, slightly acid *substance* melting at 157°, which was not analysed.

When the hydrochloride is boiled for 70 hours with dilute hydrochloric acid, it yields principally dimethylaniline with only traces of methylaniline and aniline; formic acid, quinol, tetramethylbenzidine, $C_{12}H_8(NMe_2)_2$, bisdimethylaniline, dimethyl-*p*-aminophenol, and traces of *p*-aminophenol are also formed along with a crystalline *substance* melting at 135° and having the properties of an aminophenol.

Dry dimethylaniline oxide, on being heated for 10 minutes at 140—150°, yields formaldehyde in quantity, along with dimethylaniline and methylaniline in the proportion 3 : 2, and traces of tetramethyldiaminodiphenylmethane and dimethylamino-*o*-phenol. When the oxide is heated with concentrated sulphuric acid for 12 hours at 65—75°, it suffers isomeric change to the extent of 60 per cent. into a mixture of equal parts of *o*- and *p*-dimethylaminophenol; the anhydride $(C_6H_4{\cdot}NMe_2)_2O$ of the former (Holzmann, Abstr., 1888, 1080) is also obtained, along with dimethylaniline and methylaniline, in the proportion 9 : 1.

The production of methylaniline probably takes place thus: $NPhMe_2{:}O = NHMePh + CH_2O$, the formaldehyde then interacting with dimethylaniline to form tetramethyldiaminodiphenylmethane. Aniline is formed similarly along with formaldehyde owing to oxidation of the methylaniline by oxygen derived from the dimethylaniline oxide; the dimethylaminophenols, formed from the latter by isomeric change, yield methylaminophenol and aminophenol in the same way. Quinol is formed by the hydrolysis of dimethyl-*p*-aminophenol. W. A. D.

Action of Nitric Acid on the Esters of Phenylmethylaminoformic Acid. By Pieter van Romburgh (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, **3**, 451—453).—*Methyl phenylmethylcarbamate*, obtained by the action of methylaniline on methyl chloroformate, is a crystalline substance, which melts at 44° and boils at 243°; when treated with a mixture of sulphuric and nitric acids, it yields the 2 : 4-*dinitro*-derivative, which crystallises in glossy, transparent crystals and melts at 98°; the corresponding *dinitro*-derivative of the ethyl ester melts at 112°. Both dinitro-derivatives, when heated in sealed tubes at 150° with fuming hydrochloric acid, decompose, giving carbon dioxide, alkyl chlorides, and 2 : 4-dinitromethylaniline. The corresponding 2 : 4 : 6-trinitro-compounds were obtained by the action of methyl iodide on the silver salts of the 2 : 4 : 6-trinitrophenylcarbamic esters; the *methyl* ester is a yellow, crystalline substance and melts at 112—113°, the *ethyl* ester melts at 65°. R. H. P.

Action of Toluene-*p*-sulphinic Acid on Nitrosobenzene. By Eugen Bamberger and Adolf Rising (*Ber.*, 1901, **34**, 228—241).—The following substances have been obtained by the action of toluene-*p*-sulphinic acid on nitrosobenzene dissolved in alcohol, acetic acid, or chloroform: (1) *p*-Aminophenol. (2) Aniline.

(3) p-*Aminophenol toluene*-p-*sulphonate*, $OH{\cdot}C_6H_4{\cdot}NH_2,C_6H_4Me{\cdot}SO_3H$, which can also be prepared from *p*-aminophenol and toluene-*p*-sulphonic acid; it forms glistening, silvery-white flakes, melts and decomposes to a violet oil at 245°, dissolves readily in water and alcohol, less readily in other solvents, and yields *p*-aminophenol when acted on by sodium hydroxide.

(4) p-*Aminophenyl toluene*-p-*sulphonate*, $C_6H_4Me\cdot SO_2\cdot O\cdot C_6H_4\cdot NH_2$, was obtained as its *toluene*-p-*sulphonate*, $C_6H_4Me\cdot SO_3\cdot C_6H_4\cdot NH_2,C_7H_7\cdot SO_3H$, in the form of white needles melting at 242·5—243° to a violet liquid; the *ester* itself crystallises from alcohol in long, glassy prisms, forms a crystalline *hydrochloride*, *oxalate*, and *sulphate*, is hydrolysed only with great difficulty to *p*-aminophenol and toluenesulphonic acid, has also been prepared synthetically by reducing the corresponding nitro-ester, and is probably formed by isomeric change from an unstable additive product, $C_6H_4\cdot NH\cdot O\cdot SO_2\cdot C_6H_4Me$, of nitrosobenzene, and the sulphinic acid. The *monoacetyl* derivative, $NHAc\cdot C_6H_4\cdot O\cdot SO_2\cdot C_6H_4Me$, crystallises from benzene in flat, white, glistening needles and melts at 145·5—146°; the *diacetyl* derivative, $NAc_2\cdot C_6H_4\cdot O\cdot SO_2\cdot C_6H_4Me$, crystallises from alcohol, melts at 101°, and is converted into the preceding compound by hot aqueous sodium hydroxide. When diazotised, the ester condenses with β-naphthol to form a *compound*, $OH\cdot C_{10}H_6\cdot N_2\cdot C_6H_4\cdot O\cdot SO_2\cdot C_6H_4Me$, which crystallises in glistening, orange-red needles, and melts at 157—157·5°.

(5) β-Tolylsulphonyl-β-phenylhydroxylamine,

$$C_6H_5\cdot N(OH)\cdot SO_2\cdot C_6H_4Me,$$

a stable additive product of nitrosobenzene and the sulphinic acid, forms white, glistening plates, melts at 143—143·5°, and is identical with the substance prepared by Bretschneider (Abstr., 1897, i, 421) from β-phenylhydroxylamine and toluene-*p*-sulphinic acid, and with the synthetical product prepared from β-phenylhydroxylamine and toluenesulphonic chloride.

(6) *pp*-Toluenedisulphoxide, $C_6H_4Me\cdot SO_2\cdot S\cdot C_6H_4Me$, which is only produced in small quantities, and is identical with the substance prepared by Otto and Gruber from toluenesulphinic acid and water.

(7) A neutral substance, which formed straw-yellow crystals, melted at 161—162°, and is probably an oxy-compound.

p-*Nitrophenyl toluene*-p-*sulphonate*, $C_6H_4Me\cdot SO_2\cdot O\cdot C_6H_4\cdot NO_2$, prepared by the action of toluene-*p*-sulphonic chloride on sodium *p*-nitrophenoxide in alcoholic solution, forms square, glistening tablets, melts at 97—97·5°, and is reduced by stannous chloride and hydrochloric acid to the amino-ester already described. The o-*nitro-ester* forms compact, glassy prisms and melts at 81·5°; the o-*amino-ester* forms hard, white, glassy needles and melts at 101—101·5°. T. M. L.

Action of *p*-Tolylsulphinic Acid on β-Phenylhydroxylamine. By EUGEN BAMBERGER and ADOLF RISING (*Ber.*, 1901, **34**, 241—253. Compare Bretschneider, Abstr., 1897, i, 421).—The products of the action of toluene-*p*-sulphinic acid on β-phenylhydroxylamine are similar to those obtained from nitrosobenzene, but include also *p*-aminophenyl-*p*-tolylsulphone; this is probably due to the conversion of the hydroxylamine into nitrosobenzene and aniline, the formation of azoxybenzene being prevented by the presence of the sulphinic acid.

p-Tolylaminophenylsulphone, $NH_2\cdot C_6H_4\cdot SO_2\cdot C_6H_4Me$, forms silky, white needles, melts at 181·5°, and can be prepared synthetically by the action of phosphoric oxide on aniline hydrochloride and toluene-*p*-sulphonic acid; the *acetyl* derivative crystallises from alcohol in white needles, melts at 198°, and dissolves readily in acetone. T. M. L.

Isomerism of Thiocyanic Esters. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1901, **132**, 57—58).—Phenyl thiocyanate, freshly prepared, gave the following results: Heat of combustion at const. vol. 7675·8 cal.; molecular heat of combustion at const. press. +1037·4 Cal.; heat of formation from elements, −63·7 Cal. The heat of formation of phenylthiocarbimide previously determined is −46·5 Cal., and hence the difference between the two isomerides is 17·2 Cal., which agrees with the difference between alkyl thiocyanates and alkylthiocarbimides. Determinations of the heat of combustion of the same specimen of phenyl thiocyanate at intervals show that in the course of a few weeks at summer temperature it changes to a large extent into phenylthiocarbimide. C. H. B.

Mechanism of the Change of Arylhydroxylamines into Aminophenols. II. By EUGEN BAMBERGER (*Ber.*, 1901, **34**, 61—68. Compare this vol., i, 140).—In support of the view that the first product in the isomeric change of phenylhydroxylamines is an unsaturated substance, $C_6H_5\cdot N\colon$, a number of reactions are quoted in which additive products are formed of the types $C_6H_5\cdot NHX$ and $HX\colon C_6H_4\colon NH$, or $X\cdot C_6H_4\cdot NH_2$. To the first type belong the formation of *o*- and *p*-aminodiphenylamine, $NHPh\cdot C_6H_4\cdot NH_2$, by the action of aniline on phenylhydroxylamine, the formation of *p*-hydroxydiphenylamine,

$$NHPh\cdot C_6H_4\cdot OH,$$

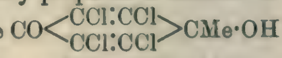
in the action of dilute sulphuric acid on phenylhydroxylamine, the formation of *p*-hydroxyphenyl-*p*-tolylamine, $C_6H_4Me\cdot NH\cdot C_6H_4\cdot OH$, by the action of phenol on *p*-tolylhydroxylamine, and the formation of a primary base, $C_{16}H_{20}ON_2$, probably $C_6H_3Me_2\cdot NH\cdot O\cdot C_6H_2Me_2\cdot NH_2$, in the action of dilute sulphuric acid on 2 : 6-dimethylphenylhydroxylamine. To the second type belong the formation of *p*-aminophenolsulphonic acid in the action of sulphuric acid on phenylhydroxylamine, $\colon N\cdot C_6H_5\rightarrow NH\colon C_6H_5\cdot O\cdot SO_3H\rightarrow NH_2\cdot C_6H_3(OH)\cdot SO_3H$, the formation of *p*-hydroxy-*p*-aminodiphenyl, $NH_2\cdot C_6H_4\cdot C_6H_4\cdot OH$, by the action of phenol on phenylhydroxylamine, and of benzidine when aniline is used, the formation of di-*p*-diaminodiphenyl ether, $O(C_6H_4\cdot NH_2)_2$, in the action of concentrated sulphuric acid on phenylhydroxylamine, and the formation of phenetidine by the action of alcoholic sulphuric acid on phenylhydroxylamine. Additional evidence of the existence of the type $C_6H_5\cdot N\colon$ is afforded by the formation of polymeric benzyleneimine, $(CH_2\colon C_6H_4\colon NH)_n$, in the action of sulphuric acid on *p*-tolylhydroxylamine, and of aminophenylnitrotolylmethane, $NH_2\cdot C_6H_4\cdot CH_2\cdot C_6H_3Me\cdot NO_2$, when *p*-nitrotoluene is also present. The products of the action of phenol on phenylhydroxylamine and *p*-tolylhydroxylamine belong to the first and second types respectively, showing that the *p*-methyl group favours the formation of compounds of the second type, as has already been pointed out in the case of the ψ-quinols (*loc. cit.*).

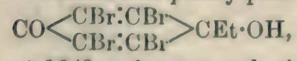
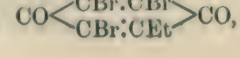
A similar explanation is given of the formation of *op*- and *pp*-dinitrodiphenylamine, $NH(C_6H_4\cdot NO_2)_2$, by the spontaneous decomposition of a solution in benzene of phenylnitrosohydroxylamine, $C_6H_5\cdot N(NO)OH$ (Abstr., 1898, i, 366), namely, the formation of *p*-nitrosophenylhydroxylamine by isomeric change of the unsaturated substance, $NO\cdot C_6H_4\cdot N\colon$ by subsequent loss of water, condensation with unchanged nitrosoamine to $NO\cdot{}_6C_6H_4\cdot NH\cdot C_6H_4\cdot N(NO)\cdot OH$, loss of HNO from the condensation product, and oxidation of the resulting dinitrosodiphenylamine to dinitrodiphenylamine; the formation of *p*-nitrodiphenylamine and its nitrosoamine would follow in a similar manner by the condensation of phenylnitrosohydroxylamine with the unsaturated substance from phenylhydroxylamine. T. M. L.

Regularities in the Distillation of Dilute Aqueous Phenol Solutions. By ALEXANDER NAUMANN and WILHELM MÜLLER (*Ber.*, 1901, **34**, 224—228).—Dilute solutions of phenol were distilled into a burette in such a way that quantities of 100 c.c. were successively collected, whilst the volume of the solution in the flask was kept constant at 500 c.c. by the gradual addition of water. It was found that the 100 c.c. of distillate always contained a constant proportion of the phenol in the flask, the mean value of the ratio being 0·335, whilst successive distillates contained proportions of phenol decreasing in a constant ratio the mean value of which was 0·665 ($=1-0·335$). The distillation of the phenol proceeds, therefore, according to the laws of an infinite geometrical progression, the sum of which represents the whole weight of phenol taken for the distillation. T. M. L.

Action of Sulphuric Acid on Phenetole. By WILLIAM B. SCHOBER and HENRY L. BOWERS (*Amer. Chem. J.*, 1901, **25**, 69—76).—When a mixture of concentrated sulphuric acid and phenetole is either left at the ordinary temperature or heated, *p*-phenetolesulphonic acid is obtained together with a small proportion of the *m*-acid, whereas according to Moody (Proc., 1892, **8**, 90, 214) only the former is produced.

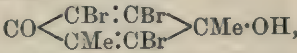
By the action of fuming sulphuric acid on phenetole at 85°, a minute quantity of phenetoledisulphonic acid is formed. E. G.

Quinols. By THEODOR ZINCKE (*Ber.*, 1901, **34**, 253—257).—Bamberger, in his account of quinols [ψ-quinols] (this vol., i, 140) has overlooked the fact that the author has already prepared a member of this class of compounds, namely, the substance  $\mathrm{CO}{<}\substack{\mathrm{CCl{:}CCl}\\ \mathrm{CCl{:}CCl}}{>}\mathrm{CMe\cdot OH}$ (Abstr., 1896, i, 214). This is obtained by oxidising tetrachloro-*p*-cresol with boiling nitric acid of sp. gr. 1·35; in the cold a nitroketone is formed which, however, yields the ψ-quinol when heated with acetic acid; on reduction with zinc and hydrobromic acid, it is reconverted into the tetrachlorocresol; it dissolves in alkalis, forms an acetyl derivative, and reacts with alkalis and with aniline, exchanging one atom of chlorine for the groups OH or NHPh respectively, and forming products that are still quinone derivatives; it does not react with phenylhydrazine.

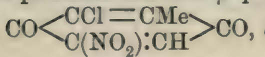
Tetrabromo-*p*-ethylphenol can also be converted into a *ψ-quinol*,  $\mathrm{CO}{<}\substack{\mathrm{CBr{:}CBr}\\ \mathrm{CBr{:}CBr}}{>}\mathrm{CEt\cdot OH}$, which melts at 140°, and its *acetyl* derivative at 124°; when treated with cold concentrated sulphuric acid, it forms yellow *tribromoethyl*-p-*quinone*,  $\mathrm{CO}{<}\substack{\mathrm{CBr{:}CBr}\\ \mathrm{CBr{:}CEt}}{>}\mathrm{CO}$, which melts at

118—120°, and can be converted into a colourless *quinol* melting at 141°.

Tetrabromo-*p*-cresol yields a *ψ-quinol*, $\mathrm{CO}<\begin{matrix}\mathrm{CBr\!:\!CBr}\\ \mathrm{CBr\!:\!CBr}\end{matrix}>\mathrm{CMe\cdot OH}$, melting at 205°; the *acetyl* derivative melts at 175—176°.

Tribromo-*m*-xylenol yields a *ψ-quinol*,  $\mathrm{CO}<\begin{matrix}\mathrm{CBr\!:\!CBr}\\ \mathrm{CMe\!:\!CBr}\end{matrix}>\mathrm{CMe\cdot OH}$, melting at 176°; the *acetyl* derivative melts at 129°. The acid character of this and of the last ψ-quinol is very feeble.

Tribromophenols are less readily oxidised to ψ-quinols by nitric acid of sp. gr. 1·4 in acetic acid solution; if the action is stopped after a short time, dibromonitrophenols are obtained. Tribromo-*p*-cresol yields a ψ-quinol, $\mathrm{CO}<\begin{matrix}\mathrm{CBr\!:\!CBr}\\ \mathrm{CBr{=}CH}\end{matrix}>\mathrm{CMe\cdot OH}$, which melts at 128°, its acetyl derivative melting at 127—128° (Abstr., 1900, i, 545). Tribromoethylphenol yields a *ψ-quinol*, $\mathrm{CO}<\begin{matrix}\mathrm{CBr\!:\!CBr}\\ \mathrm{CBr{=}CH}\end{matrix}>\mathrm{CEt\cdot OH}$, melting at 105°. Both these ψ-quinols are soluble in alkalis.

Monochloro- and monobromo-*p*-cresol are only attacked by nitric acid of sp. gr. 1·5, and the products are not ψ-quinols (Abstr., 1900, i, 545), but nitroquinones,  $\mathrm{CO}<\begin{matrix}\mathrm{CCl{=}CMe}\\ \mathrm{C(NO_2)\!:\!CH}\end{matrix}>\mathrm{CO}$, &c. C. F. B.

Derivatives of Catechol. By OSCAR WISINGER (*Monatsh.*, 1900, **21**, 1007—1020).—4-*Nitrocatechol diethyl ether*, obtained by the action of 75 per cent. nitric acid on catechol diethyl ether dissolved in glacial acetic acid, crystallises in bright yellow needles, melts at 73—75°, and, when reduced with tin and hydrochloric acid, yields the *hydrochloride* of the corresponding amino-compound; when boiled with acetic anhydride, this forms the *diacetyl* derivative, $C_6H_3(OEt)_2\cdot NAc_2$, which crystallises in transparent leaflets, melts at 120—121°, and when partially hydrolysed yields the *monoacetyl* derivative, which crystallises in white leaflets melting at 125—126°. When catechol methyl ether is nitrated in a similar manner, a mixture of 1-*methoxy*-2-*ethoxy*-4-*nitrobenzene* and 1-*ethoxy*-2-*methoxy*-4-*nitrobenzene* is obtained; one of these is soluble in alcohol, crystallises in small, yellow needles, melts at 65—67°, and, when reduced, yields the *hydrochloride* of an *amino*-compound the diacetyl and monoacetyl derivatives of which melt respectively at 117—119° and 136—138°; the other is only slightly soluble in alcohol, crystallises in long, yellow needles, melts at 100—102°, and when reduced yields the hydrochloride of an *amino*-compound the *diacetyl* and *monoacetyl* derivatives of which melt respectively at 135—137° and 142—143°.

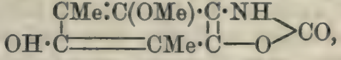
The constitution of these compounds was determined by their conversion into hydroxyquinol triethyl ether. R. H. P.

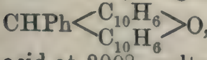
Alkyl Ethers of Phloroglucinols. II. Ethers of Methylphloroglucinol. By JOSEF HERZIG and FRANZ THEUER (*Monatsh.*, 1900, 21, 852—865. Compare Abstr., 1900, i, 545; and Reisch, Abstr., 1899, i, 803).—Methylphloroglucinol dimethyl ether is not altered by treatment with alcoholic potash, and when treated with methyl iodide and sodium is converted into the *trimethyl ether*, which is a colourless, mobile oil boiling at 140—142° under 18 mm. pressure, and solidifying at −13° to a white, crystalline mass, which melts at 10—13°; the corresponding *methylphloroglucinol dimethyl ethyl ether* is obtained as a mass of silky crystals, melts at 38°, and boils at 149—151° under 16 mm. pressure; *dibromomethylphloroglucinol dimethyl ether*, $OH \cdot C_6MeBr_2(OMe)_2$, obtained by the action of bromine on the dimethyl ether dissolved in glacial acetic acid, crystallises in needles, melts at 73—74°, and can be recovered unaltered after treatment with alcoholic potash; the formation and behaviour of these compounds show that in methylphloroglucinol dimethyl ether the third hydroxyl group is "fixed" just as in the dialkyl ethers of phloroglucinol. Tetramethylphloroglucinol methyl ether, when treated with bromine, yields dibromotetramethylphloroglucinol, which, when boiled with acetic anhydride, is converted into *acetylbromotetramethylphloroglucinol*, $C_6Me_4O_2Br \cdot OAc$, which crystallises in lustrous needles and melts at 135°. The oil, probably hexamethylphloroglucinol, obtained along with tetramethylphloroglucinol by the methylation of methylphloroglucinol methyl ether, and described by Reisch (*loc. cit.*) as pentamethylphloroglucinol, when treated with bromine yields a *compound* which crystallises in the monoclinic system [$a:b:c = 1{\cdot}373:1:1{\cdot}116$, $\alpha = 85°10'$], melts at 129—131°, and is probably bromotrimethylphloroglucinol. R. H. P.

Alkyl Ethers of the Phloroglucinols. III. Ethers of Dimethylphloroglucinol. By JOSEF HERZIG and M. HAUSER (*Monatsh.*, 1900, **21**, 866—874. Compare preceding abstract).—By a continued treatment of an alcoholic solution of dimethylphloroglucinol with hydrochloric acid, a mixture of the mono- and di-ethyl ethers is obtained. *Dimethylphloroglucinol methyl ether* is a colourless oil which boils at 185° under 13 mm. pressure; the *dimethyl* ether crystallises in colourless needles or plates, melts at 100°, is volatile with steam, and when treated with ethyl iodide and sodium yields the *trimethyl* ether which crystallises from alcohol and melts at 59°. *Trimethylphloroglucinol ethyl ether*, obtained by repeated treatment of an alcoholic solution of trimethylphloroglucinol with hydrochloric acid, is a white, crystalline powder, melts at 130°, and when treated with bromine yields tribromotrimethylphloroglucinol (Abstr., 1899, i, 32). R. H. P.

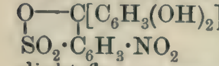
Alkyl Ethers of the Phloroglucinols. IV. Trimethyl Ether of Phloroglucinol. By JOSEF HERZIG and H. KASERER (*Monatsh.*, 1900, **21**, 875—878).—If a solution of phloroglucinol in methyl alcohol is repeatedly treated with hydrogen chloride, a small quantity of *phloroglucinol trimethyl ether* is formed; this is a white, crystalline substance, melts at 50—52°, and is volatile with steam. R. H. P.

Influence of the Substituting Radicle on the Tautomerism of Phloroglucinol [Derivatives]. By FELIX KAUFLER (*Monatsh.*, 1900, **21**, 993—1006).—When phloroglucinol dissolved in alcoholic potash is treated with benzyl chloride, a mixture of *phloroglucinol dibenzyl ether*, which is a yellow powder melting at 62—64°, and *phloroglucinol tribenzyl ether*, which is a similar substance melting at 39—41°, is obtained, and is separated by extracting the dibenzyl ether with potassium hydroxide solution. *Dimethylphloroglucinol dibenzyl ether*, which melts at 60°, and *dimethylphloroglucinol tribenzyl ether* are obtained in a similar manner from dimethylphloroglucinol. When the actions of propyl iodide and *iso*propyl iodide on phloroglucinol were compared, it was seen that the product from the reaction with *iso*propyl iodide contained a much lower proportion of the *iso*propyl radicle than did that from the reaction of propyl iodide of the propyl radicle. These and other differences previously known in the action of alkyl haloids on phloroglucinol are discussed. R. H. P.

Proof of the Position [of the Methyl Groups] in Dimethyl phloroglucinol Methyl Ether. By Carl Bosse (*Monatsh.*, 1900, **21**, 1021—1036).—Dimethylphloroglucinol methyl ether (Abstr., 1898, i, 579), when treated with amyl nitrite and potassium hydroxide in absolute alcohol, is converted into 5-*hydroxy*-3-*methoxy*-p-*xyloquinone*-4-*monoxime*, which forms red aggregates of crystals and melts and decomposes at 166·5°; when reduced with stannous chloride, it yields 4-*amino*-1 : 5-*dihydroxy*-3-*methoxy*-*xylene hydrochloride*, which crystallises in silky needles, forms a *tetracetyl* derivative melting at 137°, and, when heated with carbamide, yields 1-*hydroxy*-3-*methoxycarbonyl*-4-*aminoxylenol*,  $\begin{array}{l}\text{CMe:C(OMe)}\cdot\text{C}\cdot\text{NH} \\ \text{OH}\cdot\text{C}{=\!=\!=}\text{CMe}\cdot\text{C}-\text{O}\end{array}\!\!>\!\text{CO}$, which crystallises in flesh-coloured flakes and melts at 253—254°. When oxidised with ferric chloride, the hydrochloride is converted into 5-*hydroxy*-3-*methoxy*-p-*xyloquinone*, which crystallises in orange-coloured needles and melts at 116·5°; when reduced with stannous chloride, it yields 3-*methoxy*-2 : 6-*dimethylphentriol*, which crystallises in colourless monoclinic plates [$a : b : c = 0{\cdot}6123 : 1 : 0{\cdot}6230$, $a = 125°22'$], melts at 125°, and forms a *triacetyl* derivative melting at 76°. The oxime previously referred to forms a *sodium* salt, which crystallises in ruby-red needles, and a reddish-brown *silver* salt; both of these, when treated with ethyl iodide, yield a small quantity of a yellowish, crystalline *compound* melting at 189·5°, and the *ethyl* ether, which crystallises in slender, yellow needles, melts at 140°, and when reduced with stannous chloride yields 4-amino-1 : 5-dihydroxy-3-methoxy-xylene hydrochloride. R. H. P.

Action of β-Naphthol on Aldehydes. By John T. Hewitt and A. J. Turner (*Ber.*, 1901, **34**, 202—204. Compare Rogoff, this vol., i, 152).—*Phenyldi-β-naphtholmethane*, $\text{CHPh}(\text{C}_{10}\text{H}_6\cdot\text{OH})_2$, prepared by the action of hydrochloric acid on a solution in acetic acid of β-naphthol and benzaldehyde, crystallises from acetic acid, melts at 198° (corr.), and does not readily dissolve in any solvent but acetone. The *acetate*, $\text{CHPh}(\text{C}_{10}\text{H}_6\cdot\text{OAc})_2$, forms colourless needles, melts at 199° (corr.), and is only slightly soluble in organic solvents. The anhydride,  $\text{CHPh}\!<\!\begin{array}{l}\text{C}_{10}\text{H}_6\\ \text{C}_{10}\text{H}_6\end{array}\!\!>\!\text{O}$, prepared by heating the dinaphthol with acetic acid at 200°, melts at 191°, and is identical with the substance prepared by Claisen (Abstr., 1887, 270) and by Trzcinski (Abstr., 1884, 1185). T. M. L.

Symmetrical Chloride of *p*-Nitro-*o*-sulphobenzoic Acid. By William E. Henderson (*Amer. Chem. J.*, 1901, **25**, 1—26. Compare Remsen and Gray, Abstr., 1897, i, 477; Hollis, Abstr., 1900, i, 292).—The symmetrical chloride of *p*-nitro-*o*-sulphobenzoic acid melts at 98° (uncorr.), has a density of 1·85, and forms monoclinic crystals [$a:b:c = 0·898321:1:1·114179$, $\beta = 43°11'17''$].

By the action of methyl and ethyl alcohols on this chloride, the esters described by Kastle (Abstr., 1889, 711) are produced; the chloride of methyl *p*-nitro-*o*-sulphobenzoate, $NO_2\cdot C_6H_3(CO_2Me)\cdot SO_2Cl$, cannot, however, be obtained from the pure symmetrical chloride, but is produced when the unsymmetrical chloride is employed. *Diphenyl* p-*nitro*-o-*sulphobenzoate* melts at 119°, the *di-o-tolyl* ester at 89—90°, and the di-*p*-tolyl ester at 117°. When quinol is heated with the symmetrical chloride, 4 mols. of the former appear to react with 1 mol. of the latter with formation of a dark brown *compound*; similarly, 6 mols. of pyrogallol react with 1 mol. of the chloride. By the action of resorcinol, the *sulphone-fluorescein* of *p*-nitro-*o*-sulphobenzoic acid,  $\begin{array}{l} O\text{——}C[C_6H_3(OH)_2]_2 \\ SO_2\cdot C_6H_3\cdot NO_2 \end{array}$, is obtained as a brown powder which exhibits a slight fluorescence in alkaline solution.

p-Nitro-*o*-sulphobenzoic anilide, $NO_2\cdot C_6H_3(CO\cdot NHPh)\cdot SO_2\cdot NHPh$, crystallises in needles and melts at 222°. The *anil* melts at 183°. The *dianil*, obtained by the action of phosphorus oxychloride on the anilide, crystallises in small, yellow needles and melts at 208°; when this compound is boiled with hydrochloric acid, it is converted into the anil, whilst if heated with glacial acetic acid, the infusible anilide is produced. E. G.

***o*-Phenylsulphonebenzoic Acid and its Derivatives.** By Hall Canter (*Amer. Chem. J.*, 1901, **25**, 96—111. Compare Newell, Abstr., 1898, i, 430).—*Phenyl*-o-*tolylsulphone*, $C_6H_4Me\cdot SO_2Ph$, obtained by the action of benzene and aluminium chloride on *o*-toluenesulphonic chloride, crystallises in colourless plates, melts at 67·5—68°, is readily soluble in the usual organic solvents, and also dissolves in concentrated nitric acid, but is insoluble in hydrochloric acid or water. When oxidised with hot potassium permanganate, it yields o-*phenylsulphonebenzoic acid*, $CO_2H\cdot C_6H_4\cdot SO_2Ph$, in the form of small, colourless plates melting at 267—268°, and readily soluble in alcohol. The *barium* salt, with $3H_2O$; the *calcium* salt, with $4·5H_2O$; the *magnesium* salt, with $8H_2O$; the *strontium* and *zinc* salts, both with $3H_2O$, and the *cupric* salt, with $2H_2O$, are described. The *acid chloride*, $CO_2Cl\cdot C_6H_4\cdot SO_2Ph$, crystallises from ether or benzene in colourless plates, melts at 262·5—263·5°, and is only sparingly soluble in the usual solvents. It is not readily decomposed by cold water, and is not volatile. The *amide* crystallises in regular, transparent plates, and melts at 220—257°; the *anilide* crystallises from alcohol in glistening plates melting at 234—235°. When the acid chloride is treated with benzene and aluminium chloride, it yields *o*-benzoyldiphenylsulphone (compare Remsen and Sanders, Abstr., 1895, i, 474). J. J. S.

***o*- and *p*-Chlorophenylacetic Acid.** By H. Mehner (*J. pr. Chem.*, 1900, **62**, [ii], 554—566).—o-*Chlorophenylacetonitrile*, obtained by the action of potassium cyanide on *o*-chlorobenzyl chloride, is a colourless oil which boils at 240—242°. When the nitrile is heated with aniline, o-*chlorophenylacetylphenylamidine*, $C_6H_4Cl\cdot CH_2\cdot C(NHPh){:}NH$, is produced, which crystallises in light brown needles and melts at 117°. The *thioamide*, $C_6H_4Cl\cdot CH_2\cdot CS\cdot NH_2$ or $C_6H_4Cl\cdot CH_2\cdot C(SH){:}NH$, prepared by heating the nitrile with alcoholic ammonium sulphide, crystallises in white leaflets, melts at 137°, and is easily soluble in alcohol, ether, or hot water. The *amide*, obtained by the action of concentrated sulphuric acid on the nitrile, crystallises in white leaflets, melts at 175°, and dissolves readily in alcohol, hot water, or hot benzene, but only sparingly in ether. o-*Chlorophenylacetic acid*, $C_6H_4Cl\cdot CH_2\cdot CO_2H$, prepared by the action of nitrous acid on the amide, crystallises in white needles and melts at 95°; its *ammonium* salt is described. The *anilide*, o-*toluidide*, and p-*toluidide* crystallise in white needles and melt at 138·5°, 174°, and 169·5° respectively; the *phenylhydrazide* forms white plates and melts at 175°. The *methyl* ester boils at 125—128°, and the *ethyl* ester at 134°, under 23 mm. pressure.

p-Chlorophenylacetic acid melts at 105—106°. The *anilide* crystallises in white leaflets, and melts at 164·5°; the o-*toluidide* melts at 179°, and the p-*toluidide* at 189·5°. The *phenylhydrazide* crystallises in white needles and melts at 166°. 2 : 5-*Dinitro*-p-*chlorophenylacetic acid* crystallises in pale yellow needles and melts at 167°. *Ethyl benzoyl*-p-*chlorophenylacetate* crystallises in white needles and melts at 97—98°.

E. G.

Nitration of Mesitylenic Acid. By EUGEN BAMBERGER and ED. DEMUTH (*Ber.*, 1901, **34**, 27—33. Compare Konowaloff, Abstr., 1896, i, 673).—The authors modify the details of Schmitz's method (Abstr., 1879, 155) of preparing *a*- and *β*-nitromesitylenic acids, since this method, as formerly described, yields a mixture of two *dinitromesitylenic acids* (*a* and *β*).

a-Dinitromesitylenic acid $[Me_2:(NO_2)_2:CO_2H = 1:3:4:6:5]$ is the principal product, and yields a more soluble *barium* salt than the *β*-acid; it forms slender, colourless prisms and melts at 212·5—213° (215·5—216° corr.). On reduction with tin and hydrochloric acid, it yields 4 : 6-diamino-1 : 3-xylene (Grevingk, Abstr., 1885, 144), and, with ammonium sulphide, *nitroaminomesitylenic acid* $[Me_2:NO_2:NH_2:CO_2H = 1:3:4:6:5]$, which crystallises from water or xylene in long, lustrous, sulphur-yellow needles, from alcohol in thick, six-sided plates, and melts at 190°.

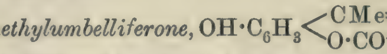
β-Dinitromesitylenic acid $[Me_2:(NO_2)_2:CO_2H = 1:3:2:4:5]$ crystallises from water or xylene in nodular aggregates of slender needles, melts at 207·5—208° (210·5—211° corr.), and on reduction with ammonium sulphide yields the corresponding *nitroaminomesitylenic acid* $[Me_2:NO_2:NH_2:CO_2H = 1:3:2:4:5$ or $1:3:4:2:5]$, which crystallises from alcohol on adding light petroleum in yellow plates and melts and decomposes at 277·5°. A small quantity of a substance melting at 175° was also obtained; this, probably, is the second nitroaminomesitylenic acid theoretically possible. *Diamino*-m-*xylene*, $[Me_2:(NH_2)_2 = 1:3:2:4]$, obtained by reducing *β*-dinitromesitylenic acid with tin and hydrochloric acid, yields a *dibenzoyl* derivative crystallising from abso-

lute alcohol in lustrous, white needles and melting at 226·5—227·5° (corr.).
W. A. D.

Condensation of α-Benzylcinnamic Acid (Benzylidenehydrocinnamic Acid) to α-Benzylidenehydrindone. By Bastian Schmid (*J. pr. Chem.*, 1900, **62**, [ii], 545—553).—α-Benzylcinnamic acid dissolves slowly in concentrated sulphuric acid with formation of a yellow solution which, when poured into water, yields a crystalline precipitate of benzylidenehydrindone (Kipping, Trans., 1894, **65**, 498) melting at 113—114°. The *oxime* crystallises from methyl alcohol in greenish-yellow masses and melts and decomposes at 184—190°; its formation is accompanied by that of another *substance* which crystallises in yellow needles and melts at 155°. The *phenylhydrazone* was also prepared.
E. G.

Coumarins from Phenols and Negatively-substituted Alkyl Acetates: Study of Coumarins. By Hans von Pechmann and Erwin Hanke (*Ber.*, 1901, **34**, 354—362).—Ethyl benzoylacetoacetate, when condensed with resorcinol in the presence of cold concentrated sulphuric acid, yields exclusively 4-phenylumbelliferone owing to the elimination of its acetyl group; the *benzoyl* derivative of the condensation product crystallises from alcohol in needles and melts at 136°.

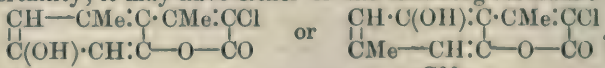
4-Methylumbelliferone results from the condensation of ethylacetylmalonate and resorcinol.

3-*Chloro-4-methylumbelliferone*,  $OH\cdot C_6H_3<{CMe \atop O\cdot CO}>C\cdot Cl$, prepared from resorcinol and ethyl α-chloroacetoacetate in the presence of cold concentrated sulphuric acid, separates from dilute alcohol in lustrous crystals containing $\frac{1}{2}H_2O$; it becomes anhydrous when heated at 105—110°, and then melts at 236°. The substance is somewhat insoluble even in boiling solvents, its solutions exhibiting a violet fluorescence; it dissolves in solutions of ammonia, and the alkali hydroxides and carbonates, being reprecipitated by carbon dioxide. On heating its alkaline solution, 6-hydroxy-3-methylcoumarilic acid and 6-hydroxy-3-methylcoumarin are produced.

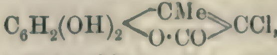
The *acetyl* and *benzoyl* derivatives of 3-chloro-4-methylumbelliferone crystallise in leaflets and melt respectively at 161° and 163°.

3-*Chlorohydroxy-4 : ?-dimethylcoumarin*, produced by condensing orcinol with ethyl α-chloroacetoacetate, crystallises in felted needles and melts at 295°; its solutions in concentrated sulphuric acid and the aqueous alkalis have a yellow colour, but no fluorescence. It differs from the preceding compound in not yielding a red coloration with ferric chloride; its *acetyl* and *benzoyl* derivatives crystallise in needles sparingly soluble in alcohol and melt respectively at 160° and 196°.

The constitution of this coumarin derivative has not been determined with certainty; it may have either of the following formulæ:



$$\begin{array}{l} CH{-}CMe{:}C\cdot CMe{:}CCl \\ C(OH)\cdot CH{:}C{-}O{-}CO \end{array} \quad \text{or} \quad \begin{array}{l} CH\cdot C(OH){:}C\cdot CMe{:}CCl \\ CMe{-}CH{:}C{-}O{-}CO \end{array}.$$

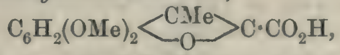
3-*Chloro-4-methyldaphnetin*,  $C_6H_2(OH)_2<{CMe \atop O\cdot CO}>CCl$, obtained by mixing an ethereal solution of ethyl α-chloroacetoacetate and excess of pyrogallol with cold concentrated sulphuric acid, crystallises from alcohol in lustrous needles and melts at 265° ; it is somewhat insoluble in the ordinary media, and its solutions do not exhibit fluorescence. The alkaline solution is yellow, and darkens on the addition of excess of solvent or on exposure to the air ; ferric chloride develops a green coloration.

The *dimethyl* ether crystallises from alcohol in felted needles and melts at 172—173° ; on boiling with alkaline solutions, it yields 6 : 7-dimethoxy-3-methylcoumarilic acid.

The *diacetyl* and *dibenzoyl* derivatives of 3-chloro-4-methyldaphnetin crystallise respectively in prisms and needles melting at 197° and 166°. 6-Hydroxy-3-methylcoumarilic acid, produced by boiling 3-chloro-4-methylumbelliferone with excess of 10 per cent. sodium hydroxide solution, is isolated by acidifying the cooled alkaline solution and purified by crystallisation from hot water ; it separates in colourless needles which at 105—110° evolve $\frac{1}{2}$ mol. of water, and melt at 226°. 6-Hydroxy-3-methylcoumarone is obtained as a bye-product in this reaction ; it melts at 103°, and does not become coloured on exposure (compare Hantzsch, Abstr., 1886, 707).

Hydroxymethyl-4-*methylcoumarone*, the main product of the action of aqueous solutions of ammonia, the alkali hydroxides, or carbonates, on 3-chlorohydroxy-4 : ?-dimethylcoumarin, crystallises from water in needles melting at 94° ; it is readily soluble in the ordinary solvents, its solution is not fluorescent and does not develop any coloration with ferric chloride. The substance, when dissolved in cold concentrated sulphuric acid, develops a reddish-yellow coloration which changes to violet on heating.

6 : 7-*Dimethoxy*-3-*methylcoumarilic acid*,



$$C_6H_2(OMe)_2{<}\overset{CMe}{\underset{O}{}}{>}C{\cdot}CO_2H,$$

obtained by boiling for 10—15 minutes 3-chloro-7 : 8-dimethoxy-4-methylcoumarin with excess of sodium hydroxide solution, crystallises from alcohol or acetic acid in lustrous leaflets and melts at 184°. In concentrated sulphuric acid, it develops a yellow coloration which changes to blue on warming.

6 : 7-*Dimethoxy*-3-*methylcoumarone*, produced by slowly distilling the preceding acid, is an oil which remains liquid at −5° and boils at 142° under 25 mm., and at 273° under the ordinary pressure ; it is soluble in the ordinary solvents, and volatile in steam. Its solution in concentrated sulphuric acid is yellow and becomes blue on warming.

G. T. M.

Pseudo-acid Derived from Agaric. By L. ALPHONSE ADRIAN and AUGUSTE TRILLAT (*Compt. rend.*, 1901, **132**, 151—152).—The *compound*, $C_{39}H_{60}O_6$, obtained by extracting powdered agaric with dilute alcohol, evaporating to dryness, and crystallising the product successively from benzene and alcohol, crystallises in needles melting at 258° (corr.); when exposed to moist air, the melting point falls to 240°. The molecular weight, determined in acetic acid solution by the ebullioscopic method, is 632, the calculated value being 624. The substance is not acidic and is only slightly soluble in sodium hydroxide solution ; it dissolves in concentrated sulphuric acid without alteration, the solution having a yellow colour which changes to orange-purple on adding a trace of nitric acid.

Fusion with potash decomposes the compound, yielding two definite products, the first a liquid boiling at 180—190° and having the properties of an unsaturated aliphatic acid, the second a neutral, pungent, aromatic oil yielding a nitro-derivative slowly decomposing at 50° but melting at 100° when rapidly heated.

The nitro-compound is insoluble in solutions of the alkalis and alkali carbonates; on reduction, it yields a diazotisable amine, the diazonium salt of which, when combined with *R*-salt gives rise to a reddish-brown azo-colouring matter.

Oxidation of the compound $C_{39}H_{60}O_6$ by chromic acid furnishes a product crystallising in white leaflets softening at 175° and melting at 185°; this substance is insoluble in solutions of the alkalis but dissolves in concentrated sulphuric acid without alteration; it contains C, 69·11, and H, 8·47 per cent. G. T. M.

Filicitannic Acid. By R. Reich (*Arch. Pharm.*, 1900, **238**, 648—671).—Filicitannic acid is a glucoside contained in *Extractum Filicis maris spirituosum spissum* to the extent of 5—6 per cent.; it can be obtained from this extract by digesting with cold 10 per cent. alcohol and precipitating the filtered solution with lead acetate; it is set free from the lead precipitate by hydrogen sulphide. It is contained to the extent of 2·7 per cent. in the dried roots or rhizomes, and can be extracted directly from these with 10 per cent. alcohol; water extracts only 0·4 per cent. The substance has a faintly acid reaction; with ferric chloride, it gives a green coloration, changed to violet, and then red, by the addition of a very little sodium carbonate; it has but little reducing action on Fehling's solution or on alkaline silver salts, and in alkaline solution it is oxidised but very slowly by the air.

Filicitannic acid appears to have the composition $C_{82}H_{72}O_{36}N_2,2H_2O$, or $C_{82}H_{76}O_{38}N_2$; its amorphous, insoluble *barium*, *calcium*, and *magnesium* salts, $C_{82}H_{70}O_{38}N_2Ba_3$, &c., were analysed. It forms a *benzoyl* derivative, $C_{82}H_{73}O_{38}N_2Bz_3$, which carbonises slowly above 200°. When dissolved in 2 per cent. aqueous potassium hydroxide and treated with bromine, it forms an orange-red *bromo*-derivative, $C_{82}H_{64}O_{38}N_2Br_{12}$. When treated with chlorine in the same way, it is at once chlorinated, oxidised, and hydrolysed (a sugar being eliminated); the product is orange-yellow, and has the composition $C_{76}H_{48}O_{30}N_2Cl_{12}$. When the acid is hydrolysed with aqueous sulphuric, hydrochloric, or hydriodic acid, a sugar is eliminated, and red, amorphous "filix-red" is formed; this appears to be a mixture, for it is only partly soluble in alcohol. If the hydrolysis is effected with 2 per cent. alcoholic hydrochloric acid at 100°, a red, amorphous *ethyl ether*, $C_{76}H_{59}O_{29}N_2\cdot OEt$, is obtained; this yields the same product when chlorinated as filicitannic acid does, and forms violet *magnesium* and *calcium* salts, $C_{78}H_{58}O_{30}N_2Mg_3$, &c. The *sugar* could not be obtained crystalline, nor could a crystalline derivative of it be prepared; it could not be identified with certainty, but there is a possibility that it may be dextrose. When filicitannic acid is boiled with 15 per cent. aqueous sodium hydroxide and zinc powder, and when it is treated with alkali under other circumstances, phloroglucinol and protocatechuic acid are formed in small quantity; the main product of the reaction escaped detection, however. When the acid is oxidised with alkaline permanganate, or with nitric acid, large quantities of oxalic acid are formed; no other product could be detected. C. F. B.

Condensation of *iso*Butaldehyde with Aromatic Orthoaldehydes. By O. Herzog and O. Kruh (*Monatsh.*, 1900, **21**, 1095—1110). —*iso*Butaldehyde (Fossek, Abstr., 1884, 37) and salicylaldehyde react in the presence of dilute potassium carbonate solution or in a mixture of acetic and hydrochloric acids, yielding the unstable *aldol*,

$$OH\cdot C_6H_4\cdot CH(OH)\cdot CMe_2\cdot CHO;$$

this is a colourless oil with a phenolic odour, is sparingly soluble in water, but readily in ether or chloroform; it reduces ammoniacal silver nitrate, and when distilled under reduced pressure is resolved into its constituents. Its *oxime*, $C_{11}H_{15}O_2N$, is a pale yellow syrup, and shows few of the characteristics of oximes. When the aldol is treated with potassium permanganate by Zeisel's method, it is partly oxidised to a mixture of salicylic and *iso*butyric acids; with chromium trioxide, it yields a small amount of a compound melting at 64—66°, probably o-*hydroxy*iso*butyrophenone*, $OH\cdot C_6H_4\cdot CO\cdot CHMe_2$. Alcoholic potash converts a mixture of the two aldehydes into potassium salicylaldehyde, Fossek's glycol (*loc. cit.*), and *iso*butyric acid.

o-Ethoxybenzaldehyde (Löw, Abstr., 1892, 57) and *iso*butaldehyde react under the influence of alcoholic potash to yield the *glycol*, $OEt\cdot C_6H_4\cdot CH(OH)\cdot CMe_2\cdot CH_2\cdot OH$, as a yellowish oil distilling at 203—205° under 16 mm. pressure, and yielding a *diacetate* which distils at 192—193° under 17 mm. pressure.

The *methoxyglycol*, $OMe\cdot C_6H_4\cdot CH(OH)\cdot CMe_2\cdot CH_2\cdot OH$, distils at 185—186° under 16 mm., and its *diacetate* at 187° under 18 mm. pressure.

When potassium carbonate solution is used as the condensing agent, the aldol, $OEt\cdot C_6H_4\cdot CH(OH)\cdot CMe_2\cdot CHO$, is formed; it crystallises from acetone, melts and decomposes at 190—193°, is readily soluble in chloroform, and when reduced with aluminium amalgam gives the glycol described above.

The *glycol*, $NO_2\cdot C_6H_4\cdot CH(OH)\cdot CMe_2\cdot CH_2\cdot OH$, is formed by the action of alcoholic potash on *o*-nitrobenzaldehyde and *iso*butaldehyde. After some 20 crystallisations from boiling toluene, it melts at 75°.

J. J. S.

Preparation of Aminohydroxy- and Chloroaminohydroxyketones. By Franz Kunckell (*Ber.*, 1901, **34**, 124—129. Compare Abstr., 1900, i, 664).—Phenacetin readily reacts with acetyl bromide in presence of aluminium chloride to form *acetylaminohydroxyacetophenone*, $NHAc\cdot C_6H_3(OH)\cdot COMe$, which crystallises in yellow cubes melting at 165°. The orientation of the acetyl group thus introduced has not yet been definitely ascertained, but it is probable that it takes the *o*-position to the hydroxyl. The *phenylhydrazone* melts at 207°, and the *oxime* at 160°. It is converted by nitration in acetic acid solution into *nitroacetylaminohydroxyacetophenone*, $NHAc\cdot C_6H_2(OH)(NO_2)\cdot COMe$, which crystallises in yellow needles melting at 170°.

The *sodium* derivative of acetylaminohydroxyacetophenone,

$$C_{10}H_{10}O_3NNa,$$

crystallises in lemon-yellow plates, melts and decomposes at 225°, and is converted by ethyl iodide into *acetylaminoethoxyacetophenone*, which crystallises in white needles melting at 155°. This substance is sometimes formed by the action of aluminium chloride on phenacetin and acetyl bromide, instead of the hydroxy-compound. When the ethoxy-compound is heated with hydrochloric acid, it yields *ethoxyaminoacetophenone* (acetyl-*p*-phenetidine), $OEt\cdot C_6H_3(NH_2)\cdot COMe$, which forms yellow needles melting at 60°. The *hydrochloride* melts at 215°, and the *phenylhydrazone* crystallises in brownish-yellow needles which decompose at 180°. *Nitroacetylaminoethoxyacetophenone* melts at 125°.

Acetylaminohydroxyacetophenone is converted by hydrochloric acid into *hydroxyaminoacetophenone* (acetyl-*p*-aminophenol),

$$OH\cdot C_6H_3(NH_2)\cdot COMe,$$

which crystallises in yellowish needles melting at 105°, and forms a *hydrochloride* which melts and decomposes at 155°. Phenacetin is converted by chloroacetyl chloride in presence of aluminium chloride into *ω-chloroacetylaminohydroxyacetophenone*, $CH_2Cl\cdot CO\cdot C_6H_3(OH)\cdot NHAc$, which crystallises in yellow needles melting at 190°. Hydrochloric acid converts it into *ω-chloroaminohydroxyacetophenone*,

$$CH_2Cl\cdot CO\cdot C_6H_3(OH)\cdot NH_2,$$

which crystallises in yellowish-green needles, and melts at 135°. Alkalis yield with this substance an intensely red-coloured solution from which a compound of the formula $C_{20}H_{14}O_6N_2$ has been isolated.

A. H.

Selenium Derivatives of Aromatic Ketones. By Franz Kunckell and Robert Zimmermann (*Annalen*, 1901, **314**, 281—295. Compare Michaelis and Kunckell, Abstr., 1898, i, 136).—*Selenoacetophenone*, $(COPh\cdot CH_2)_2Se$, prepared by heating selenoacetophenone dichloride with carbon disulphide and zinc dust in a reflux apparatus, crystallises from dilute alcohol in pale yellow needles and melts at 73°; it dissolves readily in ether and in benzene, and undergoes no change when preserved. The reduction of the dichloride is effected more rapidly by the agency of potassium selenocyanide than by zinc dust. The *phenylhydrazone*, $(NHPh\cdot N{:}CPh\cdot CH_2)_2Se$, crystallises from dilute alcohol, and soon becomes red and viscous; it sinters at about 70°, and melts between that temperature and 100°. The *dibromide*, $(COPh\cdot CH_2)_2SeBr_2$, produced when bromine is added to an ethereal solution of the ketone, forms pale yellow needles and melts at 102°.

The *di-iodide*, $(COPh\cdot CH_2)_2SeI_2$, forms lustrous, brownish needles and melts at 112°.

When selenoacetophenone dichloride is dissolved in alcohol and heated with potassium hydroxide (2 mols.), acetophenone, selenium, and benzoic acid are produced; the last-named substance probably arises from the acetophenone by the oxidising action of selenious acid, because aqueous potassium hydroxide converts selenoacetophenone dichloride into acetophenone and selenium dioxide.

Diselenoacetophenone, $(COPh\cdot CH_2)Se_2$, prepared by agitating finely divided selenoacetophenone dichloride with ether and water, separates from alcohol in lustrous, yellowish crystals and melts at 125°; hydrochloric acid precipitates selenium from the alcoholic solution, and when chlorine is passed into an ethereal solution, selenium chloride and chloroacetophenone are produced.

*Seleno-*p*-acetylacetanilide dichloride*, $(COMe\cdot NH\cdot C_6H_4\cdot CO\cdot CH_2)_2SeCl_2$, obtained from *p*-acetylacetanilide and selenium tetrachloride, is a yellow, crystalline powder which melts at 130°. *Selenomethyl anisyl ketone dichloride*, $(OMe\cdot C_6H_4\cdot CO\cdot CH_2)_2SeCl_2$, prepared from methyl anisyl ketone and selenium tetrachloride, forms white, silky needles and melts at 122°. *Selenopropiophenone dichloride*, $(COPh\cdot C_2H_4)_2SeCl_2$, formed when a solution of selenium tetrachloride in ether is heated with propiophenone, crystallises in white needles and melts at 124°. *Selenomethyl* p*-tolyl ketone dichloride*, $(C_6H_4Me\cdot CO\cdot CH_2)_2SeCl_2$, crystallises from chloroform and melts at 132°. *Selenomethyl* p*-tolyl ketone*, $(C_6H_4Me\cdot CO\cdot CH_2)_2Se$, crystallises from alcohol in slender, pale yellow needles and melts at 103°; the *phenylhydrazone* is crystalline, but has no definite melting point, and the *dibromide* forms small, white needles which melt at 112°. *Selenomethyl* m*-xylyl ketone dichloride*,

$$(C_6H_3Me_2\cdot CO\cdot CH_2)_2SeCl_2,$$

crystallises from chloroform in slender, white needles and melts at 128°. *Selenomethyl ψ-cumyl ketone dichloride*, $(C_6H_2Me_3\cdot CO\cdot CH_2)_2SeCl_2$, melts at 139°, and *selenomethyl cumyl ketone dichloride* at 119°. *Selenoacetyldiphenyl dichloride*, $(C_6H_4Ph\cdot CO\cdot CH_2)_2SeCl_2$, and *selenomethyl naphthyl ketone dichloride* melt at 136° and 116° respectively.

M. O. F.

Dichloroacetylcatechol and Dichloroacetylpyrogallol. By H. Bruhns (*Ber.*, 1901, **34**, 91—97. Compare Nencki, Abstr., 1895, i, 44).—Catechol and pyrogallol condense with dichloroacetic acid in the presence of zinc chloride, yielding respectively dichloroacetylcatechol (12 per cent.) and dichloroacetylpyrogallol (25 per cent.).

Dichloroacetylcatechol, $C_6H_3(OH)_2\cdot CO\cdot CHCl_2$ [1 : 2 : 4], crystallises in prismatic plates melting at 112° and readily soluble in the usual solvents. Its alkaline solutions rapidly turn brown on exposure to the air; with ferric chloride, it gives a green coloration, which on the addition of sodium carbonate turns red. Cotton fabrics mordanted with alumina are dyed pale yellow, or with iron a gray-green. The *phenylhydrazone*, $C_6H_3(OH)_2\cdot C(N\cdot NHPh)\cdot CH{:}N\cdot NHPh$, crystallises in glistening, yellow needles, melts at 153°, is soluble in alcohol or ether, and gradually decomposes on exposure to the air. The *semicarbazone*, $C_6H_3(OH)_2\cdot C(N\cdot NH\cdot CO\cdot NH_2)\cdot CH{:}N\cdot NH\cdot CO\cdot NH_2,H_2O$, crystallises from hot water in yellow, prismatic plates, and forms a *hydrochloride* melting at 215—217° which is decomposed by hot water.

Dichloroacetylpyrogallol, $C_6H_2(OH)_3\cdot CO\cdot CHCl_2$ [1 : 2 : 3 : 4], crystallises from water in microscopic, rhombic prisms, melts at 165—166°, and dissolves readily in most organic solvents with the exception of chloroform. Its reactions are similar to those of dichloroacetylcatechol. The *phenylhydrazone*, $C_6H_2(OH)_3\cdot C({:}N\cdot NHPh)\cdot CH{:}N\cdot NHPh$, crystallises from methyl alcohol in needles melting at 235°. A *disulphonic acid*, $C_8H_4O_4Cl_2(SO_3H)_2$, is obtained when the dichloro-compound is dissolved in concentrated sulphuric acid and then diluted with a small amount of water at 0°. The *sodium* salt forms glistening needles, the *lead*, *copper*, *zinc*, and *silver* salts coloured amorphous precipitates. J. J. S.

Action of Alkalis on Chlorinated Hydroxy-ketones. By H. Bruhns (*Ber.*, 1901, **34**, 97—100).—The author cannot confirm Cassella and Co.'s statement (D.-R. P. 89602) that hydroxygalloacetophenone is obtained by the action of dilute alkalis on chlorogalloacetophenone. The action of alkalis has been studied in closed vessels in an atmosphere of hydrogen and at different temperatures, but the only products isolated were galloacetophenone and anhydroglycogallol (Nencki, Abstr., 1895, i, 44).

No definite products have been obtained by the action of alkalis on chloroacetylcatechol, or the two dichloro-ketones previously described (compare preceding abstract).

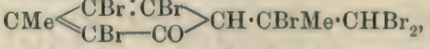
Chloroacetylcatechol reacts with semicarbazide, yielding the product $C_6H_3(OH)_2\cdot CO\cdot CH_2\cdot NH\cdot NH\cdot CO\cdot NH_2$, which crystallises in needles melting at 187°. J. J. S.

Lapachonone. III. By C. Manuelli (*Atti Real Accad. Lincei*, 1900, [v], 9, ii, 314—318).—Bromination of lapachonone in cold acetic acid solution yields:

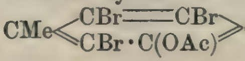
(1) *Bromolapachonone*, $C_{16}H_{15}O_2Br$, which crystallises from alcohol in small, sparkling, white prisms, melts at 126°, is slightly soluble in acetic acid, and gives the normal molecular weight in freezing benzene.

(2) A small quantity of a *bromodihydroxyquinone*, $C_{15}H_{15}O_4Br$, which is obtained as almost the sole product when the lapachonone is brominated in suspension in water. It separates from alcohol in heavy, lemon-yellow prisms which melt at 140° and dissolve in nearly all the common organic solvents, giving in freezing benzene the normal molecular weight. The *diacetyl* derivative crystallises from alcohol in thin, yellow plates melting at 132°; its *phenylhydrazone* separates from benzene as a red, crystalline crust which darkens in the air and assumes a greenish lustre recalling that of magenta, and on heating does not melt, but blackens at about 150° and afterwards decomposes; the *oxime* separates from benzene in minute red crystals which blacken at 140° but maintain their crystalline form even at 250°. T. H. P.

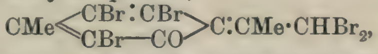
Exhaustive Bromination of Menthone. By Adolf von Baeyer and Otto Seuffert (*Ber.*, 1901, **34**, 40—53).—By the action of an excess of bromine on menthone, a crystalline product is obtained consisting chiefly of tetrabromo-*m*-cresol (10—12 per cent.) and a *compound*, $C_{10}H_8OBr_6$ (60 per cent.), analogous to Zincke's pseudoketobromides (Abstr., 1899, i, 265), to which the formula



$$CMe\begin{matrix}\diagup CBr:CBr \diagdown \\ \diagdown CBr—CO \diagup\end{matrix}CH\cdot CBrMe\cdot CHBr_2,$$

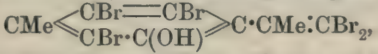
is therefore provisionally assigned; it melts and decomposes at 148—149°, crystallises from acetic acid, chloroform, or petroleum, is converted by alkalis into an intermediate red compound and then into the compounds $C_{10}H_7OBr_5$ and $C_{10}H_6OBr_4$; it also gives a red compound and loses hydrogen bromide in presence of dilute alcohol or sodium hydrogen carbonate solution or by shaking the ethereal solution with sodium hydrogen sulphite; phenylhydrazine removes hydrogen bromide without forming a hydrazone. The *acetyl* derivative, $C_{10}H_7OBr_6Ac$, prepared by the action of cold acetic anhydride and sulphuric acid, melts and decomposes at 182°, is not acted on by hot aqueous sodium hydroxide or by silver oxide, but is converted by alcoholic sodium hydroxide into tetrabromodimethylcoumarone; the formula  $CMe<\begin{array}{l}CBr{=\!=}CBr\\ CBr\cdot C(OAc)\end{array}>CMeBr\cdot CHBr_2$ is assigned to the acetate.

The first product of the action of alkalis on the compound $C_{10}H_8OBr_6$ is probably the methylenequinone,



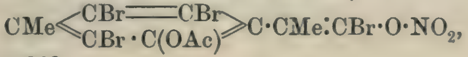
$$CMe<\begin{array}{l}CBr{:}CBr\\ CBr{-}CO\end{array}>C{:}CMe\cdot CHBr_2,$$

but this rapidly passes into *pentabromodehydrothymol*,



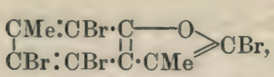
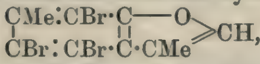
$$CMe<\begin{array}{l}CBr{=\!=}CBr\\ CBr\cdot C(OH)\end{array}>C\cdot CMe{:}CBr_2,$$

which melts at 102°, dissolves readily in alkalis and in organic solvents, and is reduced to thymol by treating successively with zinc dust and alcoholic hydrogen chloride, and with sodium and alcohol. The *acetyl* derivative, $C_{10}H_6OBr_5Ac$, prepared by the action on the preceding compound of acetic anhydride containing a little sulphuric acid, or by treating the compound $C_{10}H_8OBr_6$ with acetic anhydride, crystallises from petroleum in flat, prismatic tablets, melts at 104°, and is not acted on by aqueous alkalis, but is hydrolysed by alcoholic potassium hydroxide, losing hydrogen bromide and passing into tetrabromocoumarone; silver acetate and nitrate convert it into the *nitrate*,



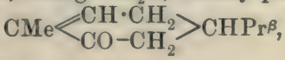
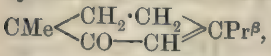
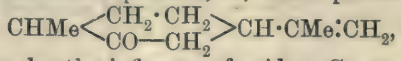
$$CMe<\begin{array}{l}CBr{=\!=}CBr\\ CBr\cdot C(OAc)\end{array}>C\cdot CMe{:}CBr\cdot O\cdot NO_2,$$

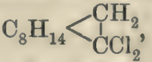
which melts at 89°.

Tetrabromodimethylcoumarone,  $\begin{array}{l}CMe{:}CBr\cdot C{-\!-}O\\ CBr{:}CBr\cdot C\cdot CMe\end{array}>CBr$, prepared by the action of alkalis on any of the preceding bromination products, crystallises from chloroform in felted needles and melts at 177—178°; it is reduced by zinc dust and alcoholic hydrochloric acid to *tribromodimethylcoumarone*,  $\begin{array}{l}CMe{:}CBr\cdot C{-\!-}O\\ CBr{:}CBr\cdot C\cdot CMe\end{array}>CH$, showing that one of the bromine atoms is in the furfuran ring; this substance crystallises from glacial acetic acid in capillary needles, and melts and decomposes at 156—147° (? 146—147°). Tetrabromodimethylcoumarone is reduced by alcohol and sodium to 2 : 5-dimethylhydrocoumarone.

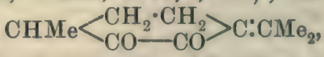
The conversion of coumarone into *o*-ethylphenol proceeds more smoothly with hydriodic acid than with alcohol and sodium (Alexander, Abstr., 1892, 1318), but the method was not successful with dimethylcoumarone.

T. M. L.

Action of Sulphuric Acid on Camphor and on Camphane Dichloride. Resolution of the Camphocean Ring. By Julius Bredt, F. Rochussen, and J. Monheim (*Annalen*, 1901, 314, 369—398).—The fact that camphor, losing $1H_2O$, readily passes into cymene, led Kekulé to his formula,  $CMe<\begin{array}{l}CH\cdot CH_2\\ CO{-}CH_2\end{array}>CHPr^{\beta}$, for the ketone, this being also in agreement with the conversion into carvacrol by means of iodine. The authors now show that in both changes carvenone,  $CMe<\substack{CH_2\cdot CH_2\\ CO-CH}>CPr^{\beta}$, is the intermediate product. The transformation of camphor into carvenone takes place under the influence of concentrated sulphuric acid at 105—110°; the unsaturated ketone is either the direct product, or, more probably, arises from dihydrocarvone,  $CHMe<\substack{CH_2\cdot CH_2\\ CO-CH_2}>CH\cdot CMe\colon CH_2$, which readily yields carvenone under the influence of acids. Carvenone has now been isolated from the more volatile constituent of camphrene, from which previous investigation had failed to remove unaltered camphor; the separation is effected by adding phenol and distilling under reduced pressure, a molecular mixture of camphor and phenol boiling at 92° under 14 mm. pressure, whilst carvenone boils at 110—111°.

Dichlorocamphane,  $C_8H_{14}<\substack{CH_2\\ |\\ CCl_2}$, also yields carvenone under the influence of concentrated sulphuric acid; it is this substance which Marsh and Gardner call camphenol (Trans., 1897, **71**, 290), whilst Marsh and Hartridge refer to it as carvenol (Trans., 1898, **73**, 852).

The experimental portion of the paper describes the production of carvenone from camphor and from dichlorocamphane, and gives details relating to the comparison of the product with carvenone.

The paper concludes with a valuable discussion of other changes involving resolution of the camphocean ring. Among these must be recognised the change which camphorquinone undergoes when treated with sulphuric acid (Manasse and Samuel, Abstr., 1899, i, 300); the product consists of the isomeric quinone,  $CHMe<\substack{CH_2\cdot CH_2\\ CO-CO}>C\colon CMe_2$, and not, as assumed by the discoverer, of the enolic modification of camphorquinone.

In the same category the authors include the transformation of calcium camphorate into camphorone, camphoric acid into *iso*lauronolic acid, and α-campholenic acid into β-campholenic acid. M. O. F.

Syntheses in the Animal Organism. II. Compounds of the Camphor Group. By HERMANN HILDEBRANDT (*Chem. Centr.*, 1901, i, 53—54; from *Arch. exp. Path. Pharm.*, 1900, **45**, 110—129).—See this vol., ii, 180.

Citraptene or Lemon Camphor. By EUG. THEULIER (*Chem. Centr.*, 1901, i, 113; from *Rev. gén. chim. pur. appl.*, **3**, 421—422).—When the terpenes of lemon oil are completely distilled in a vacuum, a residue is left from which, on cooling, pale yellow crystals of citraptene separate. The further purification of this substance has shown that it contains a substance which does not melt, together with two organic compounds which melt at 145° and 76° respectively. The compound of the higher melting point crystallises in yellow needles, whilst the other is present only in traces and separates from its solution in alcohol in an amorphous form. E. W. W.

Essential Oil from the Leaves of Alpinia Malaccensis. By PIETER VAN ROMBURGH (*Proc. K. Acad. Wetensch. Amsterdam*, 1900, **3**, 451).—The leaves of *Alpinia Malaccensis*, when distilled, yielded an oil which was principally methyl cinnamate, but also contained a terpene, the nitrosylchloride of which melted at 108° and gave pinene nitrolpiperidine when treated with piperidine (pinene nitrosyl chloride melts at 103°). R. H. P.

The Constituents of Cascarilla Oil. By GEORG FENDLER (*Arch. Pharm.*, 1900, **238**, 671—690).—Cascarilla oil is obtained from the bark of *Croton eluteria*, one of the *Euphorbiaceæ*, indigenous to the Bahamas; the sample examined had the sp. gr. 0·914 at 15°, 0·911 at 20°, and $[\alpha]_D$ 4·81° at 15°.

The oil was diluted with ether, the mixture extracted with 2 per cent. aqueous sodium carbonate, and the acids so obtained separated by means of the difference of solubility of their lead salts in ether. The insoluble portion appeared to contain palmitic and stearic acids in the proportion of about 4 to 1. The soluble portion contained an acid isomeric with undecenoic acid. This acid, *cascarillic acid*, $C_{10}H_{19}\cdot CO_2H$, melts at about −15°, boils at 270°, and has a sp. gr. 0·9324 at 20°; it is an unsaturated monobasic acid of the acrylic series; its *silver* salt was analysed. It forms an oily *bromide*, and a crystalline *amide* melting at 78°. When oxidised with fuming nitric acid, it yields an unsaturated dibasic *acid*, $C_{11}H_{18}O_4$, melting at 111°, of which the *silver* salt was analysed; it is oxidised by permanganate to lower fatty acids.

From the remaining ethereal solution, 3 per cent. aqueous potassium hydroxide extracted a mixture of phenols, consisting of eugenol mixed with a little cresol.

No aldehyde or ketone could be isolated with sodium hydrogen sulphite. No ethereal salts are present, or mixed aliphatic-aromatic ethers.

The remaining oil, freed from ether, was distilled with alcohol. The portion that distilled over was liberated by diluting the distillate with water, and fractionated. One fraction contained a terpene, $C_{10}H_{16}$, which boils at 155—157° and 90—95° under pressures of 760 and 100 mm. respectively, has a sp. gr. 0·845 at 20°, and $[\alpha]_D$ $+2·49°$ at 21°. It forms a *hydrochloride*, $C_{10}H_{17}Cl$, and a *bromide*, $C_{10}H_{16}Br_2$, both oily, and a *nitrosochloride*, $C_{10}H_{16}ONCl$, and a *nitrolpiperidide*, $NO\cdot C_{10}H_{16}\cdot C_5NH_{10}$, melting at 91—92° and 112° respectively. A second fraction consisted of cymene and limonene in the proportion of about 3 to 2. The portion that did not distil over with the alcohol was fractionated, and so separated into two sesquiterpenes, an alcohol, and a residue containing oxygen. One sesquiterpene, $C_{15}H_{24}$, boils at 255—257° and 178—181° under pressures of 1 atmo. and 100 mm. respectively, and has a sp. gr. 0·911 at 20°, and $[\alpha]_D$ $+23·49°$ at 22°. The other, $C_{15}H_{24}$, boils at 260—265° and 185—190° under pressures of 760 and 100 mm. respectively, and has a sp. gr. 0·924 at 20°, and $[\alpha]_D$ $+7·36°$ at 24°. The alcohol, $C_{15}H_{23}\cdot OH$, boils at 280—290° and 210—220° under pressures of 760 and 100 mm. respectively, and has a sp. gr. 0·977 at 20°, and $[\alpha]_D$ $-7·30°$ at 24°; oily *acetyl* and *benzoyl* derivatives were prepared.

Cascarilla oil contains, in 100 parts: cascarillic acid, 2·0; palmitic acid, 0·08; stearic acid, 0·02; eugenol (and cresol), 0·30; terpene, 10·0; *l*-limonene, 8·8; cymene, 13·2; sesquiterpene (255—257°), 10·5; sesquiterpene (260—265°), 33·0; alcohol, 11·0; high boiling fraction containing oxygen, 10·0; resin, 1·1 parts. C. F. B.

Essential Oil of Jasmine Blossom. V. By ALBERT HESSE (*Ber.*, 1901, **34**, 291—296. Compare Abstr., 1900, i, 454, &c.).—In the 'enfleurage' of jasmine blossoms, more than 9 times as much essential oil is obtained as when the blossoms are extracted with volatile solvents. The properties of the oil obtained only from jasmine blossoms are the same as those of the oil from good commercial pomades, examined previously. Essential oil of jasmine blossom contains methyl anthranilate as a normal constituent; this appears to be formed in the 'enfleurage,' however. Small quantities of a base, resembling pyridine in character, are also present. C. F. B.

Essential Oil from Ocimum Basilicum. By PIETER VAN ROMBURGH (*Proc. K. Acad. Wetensch. Amsterdam*, 1900, **3**, 454—455).—The leaves of the variety of *Ocimum basilicum*, called locally Selasih hidjau, yield methylchavicol when distilled; those from the variety Selasih besar yield eugenol and a terpene, "*ocimene*," which is an agreeably smelling, optically inactive liquid, boils at 73—74° under 21 mm. pressure, has a sp. gr. 0·794 at 22° and 0·801 at 15°, and n_D 1·4861; ocimene readily absorbs oxygen and resinifies. Under the ordinary pressure, it boils at 176—178° and, as also when heated in an atmosphere of carbon dioxide, is gradually converted into a liquid boiling at 195° and possessing a higher sp. gr. and stronger refraction. R. H. P.

Natural Resins [Ueberwallungsharze]. VII. By MAX BAMBERGER and EMIL VISCHNER (*Monatsh.*, 1900, **21**, 949—956).—The liquid obtained by the dry distillation of pinoresinol (Abstr., 1898, i, 89) separates into an aqueous layer, which contains an undetermined aldehyde and an oily layer. When this oil is distilled under reduced pressure, guaiacol, creosol, *iso*eugenol and an oil, which is probably propylpyrogallol methyl ether, are obtained from successive fractions. R. H. P.

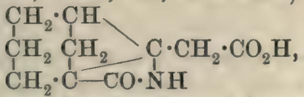
The Resin Balsam of Pinus Pinaster (Bordeaux Turpentine). By ALEXANDER TSCHIRCH and ED. BRÜNING (*Arch. Pharm.*, 1900, **238**, 630—648).—From a solution of the turpentine in ether, 1 per cent. aqueous ammonium carbonate extracts monobasic *pimarinic acid*, $C_{14}H_{22}O_2$, an amorphous substance melting at 118—119°. Aqueous sodium carbonate of 1 per cent. strength then extracts a mixture of acids, from the solution of which in methyl alcohol a relatively large amount of monobasic *pimaric acid*, $C_{20}H_{30}O_2$, crystallises; this melts at 144—146°; its *potassium*, *calcium*, *lead*, and *silver* salts were analysed. From the mother liquor of this acid, alcoholic lead acetate precipitates the lead salt of *a-pimarolic acid*, whilst that of *β-pimarolic acid* remains dissolved; these isomeric monobasic acids, $C_{18}H_{26}O_2$, are amorphous, and melt at 90—91° and 89—90° respectively. All these acids give the colour reactions of the cholesterols.

From the residual ethereal solution, the ether is distilled off, and the residue distilled with steam. An *ethereal oil* comes over; this, when distilled, yields an oil that smells like turpentine, boils at 150—175°, and has a sp. gr. 0·855 at 15°, together with a small residue of higher boiling point, which readily turns to resin. *Bordoresen* is obtained as a residue in the steam distillation; it has a viscid consistency.

The drug also contains small quantities of an *alkaloid*, and of a *colouring matter*. It has a feeble acid reaction in alcoholic solution; it neutralises no more alkali on boiling than in the cold; it contains no methoxyl group; when distilled, it yields small quantities of succinic, formic, and acetic acids.

In 100 parts of the drug there are contained: pimarinic acid, 6—7; pimaric acid, 8—10; α- and β-pimarolic acids, 48—50; ethereal oil, easily volatile, 25—26, difficultly volatile, 3—4; resen, 5—6; succinic acid, alkaloid, colouring matter, water, and impurities, 1—2 parts.

The substances described are closely related to those obtained from Jura turpentine (this vol., i, 91). Pimaric acid is quite distinct from abietic acid; curiously enough, pimaric acid was obtained from a sample of commercial American colophonium, although an authentic resin from *Pinus palustris* was found to contain only abietic acid. The solubility of various resens in 80 per cent. aqueous chloral hydrate was also studied: canadoresen, juroresen, bordoresen, abietoresen, myroxin, β-dammaroresen, and α-alban are insoluble, whilst the others are soluble, either in the cold or on heating. The resin acids dissolve with difficulty in the cold, very readily on heating. When French turpentine oil is exposed to the air for a long time in a thin layer, but very little of a resinolic acid is formed; the main product is a resen, $C_{20}H_{34}O$, which melts at 120—130°, is homologous with juroresen, and resembles bordoresen in character. C. F. B.

Nitrogen Derivatives of Cantharidin. By HANS MEYER (*Monatsh.*, 1900, **21**, 965—980).—Cantharidinimide (Abstr., 1891, 1243),  $\begin{array}{lll} CH_2\cdot CH & & \\ CH_2\ \ CH_2 & & C\cdot CH_2\cdot CO_2H \\ CH_2\cdot C & — & CO\cdot NH \end{array}$, is easily obtained by boiling cantharidin with ammonia, and forms a *potassium* salt, which crystallises in lustrous leaflets, and when treated with ethyl iodide yields cantharidinethylimide (*loc. cit.*). When the dimethyl ester of cantharidin is heated under pressure with aqueous ammonia, it is converted into a mixture of cantharidinimide and cantharidinmethylimide. The paper concludes with a discussion of the formula of cantharidinphenylhydrazide. R. H. P.

Anthophaein, the Brown Colouring Matter of Flowers. By M. MÖBIUS (*Chem. Centr.*, 1901, i, 190—191; from *Ber. bot. Ges.*, 1900, **18**, 341—347).—The pigment contained in the black portions of the flowers of *Vicia faba* cannot be extracted by alcohol, ether, chloroform, or light petroleum, but is removed by hot water. The aqueous solution of this compound, which is named anthophaein, does not exhibit a characteristic spectrum, but forms brown precipitates with acetic, hydrochloric, nitric, sulphuric, or chromic acid. Unlike phycophain, anthophaein may be precipitated from its aqueous solution by means of sodium chloride, magnesium sulphate, or calcium chloride.

E. W. W.

Metachlorophyllins and the Plurality of Chlorophyllins. By M. Tsvett (*Compt. rend.*, 1901, **132**, 149—150).—When chlorophyll is extracted with benzene-alcohol (80 per cent.), the alcoholic extract exhibits in its spectrum only that portion of the characteristic chlorophyll band in the blue, that in the yellow, due to chlorophyllin blue, being absent; in the complete chlorophyll spectrum, it is the latter segment which predominates. These results indicate that chlorophyll contains at least two chlorophyllins.

When lime, elder, or rose leaves are macerated with alcohol, ether, chloroform, or benzene and then extracted with alcohol, the chlorophyllins in solution undergo a peculiar change and become quite insoluble in benzene, this solvent scarcely extracting any colour from the alcoholic tincture. This transformation is very rapid, and in the case of lime leaves is complete in five minutes. Dark green crystals, similar to those observed by Borodin by microchemical methods, separate on evaporating the alcoholic solution.

The names *metachlorophyllins* and *metachlorophyllin-β* are proposed for the modified chlorophyllins and the crystalline product respectively.

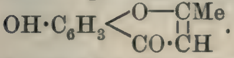
G. T. M.

Nitrofurfuran. By R. Marquis (*Compt. rend.*, 1901, **132**, 140—142).—*Nitrofurfuran*, $C_4OH_3 \cdot NO_2$, is obtained by nitrating furfuran dissolved in acetic anhydride at temperatures below $-5°$, adding the product to water, and extracting with ether containing pyridine, evaporating off the solvent under diminished pressure, and distilling the residue in a current of steam; it crystallises from light petroleum and melts at 28°. The compound has an odour resembling that of nitrotoluene; it readily dissolves in the organic solvents and in aqueous solutions of alkali hydroxides, in the latter case giving an orange solution.

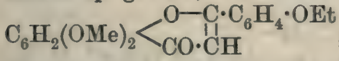
The pyridine is added to the ethereal extract in order to neutralise traces of acetic and nitric acids, and also to ensure the isolation of the nitrofurfuran. When this base is not present, the final product is an oil which reduces Fehling's solution and ammoniacal silver nitrate, and combines with phenylhydrazine, yielding a compound melting at 240°. The oily substance is not distillable in steam, and when treated with boiling water it evolves nitrous fumes and yields a soluble substance with similar reducing action which gives with phenylhydrazine a compound melting at 230°. Nitrofurfuran has no reducing action and does not combine with phenylhydrazine in the cold, although combination takes place on long boiling in acetic acid solution. The oily substance, when treated with pyridine, is converted into nitrofurfuran, and the inverse transformation is effected by the action of alkalis or dilute acids.

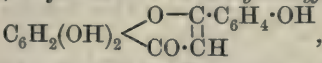
G. T. M.

Formation of Chromone Derivatives. By Stanislaus von Kostanecki and A. Różycki (*Ber.*, 1901, **34**, 102—109. Compare Nagai, Abstr., 1892, 845; Tahara, *ibid.*, 846).—Bloch and Kostanecki's

7-ethoxy-2-methylchromone (Abstr., 1900, i, 308) is obtained when Tahara's dehydroacetylresacetophenone is ethylated, and when 7-hydroxy-2-methylchromone is methylated, Nagai's dehydroacetylpæonol is formed; from these data, the authors conclude that dehydroacetylresacetophenone is identical with 7-hydroxy-2-methylchromone,  $OH\cdot C_6H_3<\begin{matrix}O-CMe\\ \quad\ \ \| \\ CO\cdot CH\end{matrix}$. Dehydrodiacetylresacetophenone is probably 3-acetyl-7-hydroxy-2-methylchromone; at all events, the acetyl group is attached to carbon and not to oxygen, as there is a free hydroxyl group present.

3-*Acetyl*-7-*ethoxy*-2-*methylchromone* crystallises from dilute alcohol in yellowish plates melting at 130°. 7-*Acetoxy*-2-*methylchromone* forms small, thick crystals melting at 94—95°. J. J. S.

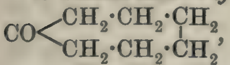
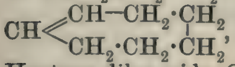
5 : 7 : 3′-Trihydroxyflavone. By STANISLAUS VON KOSTANECKI and J. STEUERMANN (*Ber.*, 1901, **34**, 109—112).—2 : 4 : 6-*Trimethoxybenzoyl*-3′-*ethoxyacetophenone*, $C_6H_2(OMe)_3\cdot CO\cdot CH_2\cdot CO\cdot C_6H_4\cdot OEt$, produced by the action of phloracetophenone trimethyl ether on ethyl *m*-ethoxybenzoate in presence of metallic sodium, crystallises in faintly yellow plates, melting at 100—101°. When treated with warm hydriodic acid of sp. gr. 1·7, it is converted into 5 : 7-*dimethoxy*-3′-*ethoxyflavone*,  $C_6H_2(OMe)_2<\begin{matrix}O-C\cdot C_6H_4\cdot OEt\\ \| \\ CO\cdot CH\end{matrix}$, which crystallises in silky, white needles melting at 151—152°. When this compound is boiled with concentrated hydriodic acid, it yields 5 : 7 : 3′-*trihydroxyflavone*,

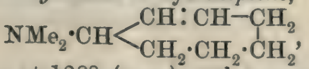


$$C_6H_2(OH)_2<\begin{matrix}O-C\cdot C_6H_4\cdot OH\\ \| \\ CO\cdot CH\end{matrix},$$

which crystallises in microscopic needles melting at 299°, and is readily soluble in alcohol, the solution being coloured red by ferric chloride. The *triacetyl* derivative crystallises in needles and melts at 165—166°.
A. H.

Synthesis of Tropidine. By RICHARD WILLSTÄTTER (*Ber.*, 1901, **34**, 129—144).—The complete synthesis of tropidine has been carried out from suberone as a starting point.

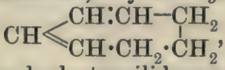
I. *Conversion of Suberone into* cyclo*Heptatriene.*—Suberone,  $CO<\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\ | \\ CH_2\cdot CH_2\cdot CH_2\end{matrix}$, can readily be converted into *cyclo*heptene,  $CH<\begin{matrix}CH-CH_2\cdot CH_2\\ | \\ CH_2\cdot CH_2\cdot CH_2\end{matrix}$, which can also be obtained from cocaine. *cyclo*Heptene dibromide, $C_7H_{12}Br_2$, is converted by dimethylamine in benzene solution into *dimethylamino*-Δ^2-cyclo*heptene*,



$$NMe_2\cdot CH<\begin{matrix}CH:CH-CH_2\\ | \\ CH_2\cdot CH_2\cdot CH_2\end{matrix},$$

which is an oil boiling at 188° (corr.) and possessing a narcotic and penetrating odour. The *platinichloride* forms prisms, and melts and decomposes at 177—178°; the *aurichloride* melts at 94—95°, the *picrate* at 162—163°, and the *methiodide* also at 162—163°. The base combines with hydrogen chloride and with bromine, forming compounds which do not pass into ammonium compounds when heated.

The same compound is formed by the action of dimethylamine on *cyclo*heptadiene monohydrobromide, and by the methylation of the amino-Δ^2-*cyclo*heptene produced by the action of bromine and an alkali on Δ^2-*cyclo*heptenecarboxylamide. When *cyclo*heptenetrimethylammonium hydroxide is distilled, it yields *cyclo*heptadiene,

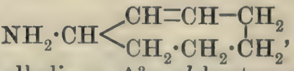


$$\mathrm{CH}<\begin{matrix}\mathrm{CH{:}CH{-}CH_2}\\ \mathrm{CH\cdot CH_2\cdot CH_2}\end{matrix},$$

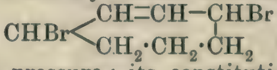
which is identical with the hydrotropilidene prepared from tropan, and is yielded by all the three known dimethylamino*cyclo*heptenes (methyltropans).

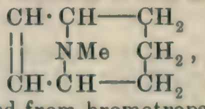
The same *cyclo*heptadiene can be prepared from Δ^2-*cyclo*heptenecarboxylic acid, which can itself be obtained from cocaine, or indirectly from suberone.

Δ^1-*cyclo*Heptenecarboxylic acid (prepared from hydroxysuberancarboxylic acid) unites with hydrogen bromide to form β-bromo*cyclo*heptanecarboxylic acid boiling at 167—168° under 25 mm. pressure, which on heating with quinoline yields a small amount of the Δ^2-acid along with the Δ^1-acid. The identity of the acid derived from these different sources was proved by its conversion into *γ-hydroxy*cyclo*heptanecarboxylolactone*, $C_8H_{12}O$, which crystallises in prisms melting at 103—104°.

Amino-Δ^2-cyclo*heptene*,  $\mathrm{NH_2\cdot CH}<\begin{matrix}\mathrm{CH{=}CH{-}CH_2}\\ \mathrm{CH_2\cdot CH_2\cdot CH_2}\end{matrix}$, is formed by the action of bromine and an alkali on Δ^2-*cyclo*heptenecarboxylamide, and is a mobile oil of strongly basic properties boiling at 166° (corr.). The *hydrochloride* melts and decomposes at 172—174°, the *platinichloride* at 208—210°, and the *aurichloride* at 120—121°; the *phenylthiocarbamide* melts at 129·5—130°. This base is converted by methylation into the methiodide of dimethylamino-Δ^2-*cyclo*heptene, which has been already described.

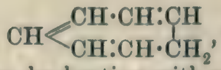
An isomeric *amino*cyclo*heptene* is formed by the reduction of tropilenephenylhydrazone, and yields a *platinichloride* which melts and decomposes at 227—229°, and a *phenylthiocarbamide* which melts at 124—125°. Its constitution has not yet been ascertained.

cyclo*Heptadiene dibromide*,  $\mathrm{CHBr}<\begin{matrix}\mathrm{CH{=}CH{-}CHBr}\\ \mathrm{CH_2\cdot CH_2\cdot CH_2}\end{matrix}$, is a viscid oil boiling at 123° under 15 mm. pressure; its constitution is shown by the fact that methylamine converts it into iso*tropidine*,



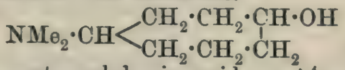
$$\begin{array}{lll}\mathrm{CH\cdot} & \mathrm{CH} & \mathrm{CH_2}\\ \| & \mathrm{NMe} & \mathrm{CH_2},\\ \mathrm{CH\cdot} & \mathrm{CH} & \mathrm{CH_2}\end{array}$$

which can also be obtained from bromotropan methobromide by heating with alkalis.

*cyclo*Heptatriene,  $\mathrm{CH}<\begin{matrix}\mathrm{CH\cdot CH{:}CH}\\ \mathrm{CH{:}CH\cdot CH_2}\end{matrix}$, can be obtained from the dibromide in two ways, by heating with quinoline, or by treatment with methylamine and exhaustive methylation of the resulting *tetramethyldiamino*cyclo*heptene*, which boils at 225—235°. The hydrocarbon thus obtained is identical with the tropilidene prepared from tropidine.

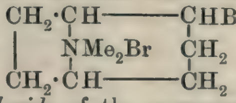
II. *The Monocyclic Tropine Bases.*—Dimethylamino*cyclo*heptadiene is formed by the action of dimethylamine on tropilidene monohydrobromide, and is identical with α-methyltropidine. *Tropilidene dihydrobromide*, $C_7H_{10}Br_2$, boils at 125—126° under 15 mm. pressure, and differs from *cyclo*heptadiene dibromide. The *monohydrobromide* boils at 74—75° under 8—9 mm. pressure, and has a sp. gr. 1·4003 at 14°/4°. Three of the isomeric methyltropans can also be synthetically prepared.

Δ^2-Methyltropan has already been described as dimethylamino*cyclo*heptene. Δ^4-*Methyltropan* formed by the reduction of α-methyltropidine in alcoholic solution with sodium, boils at 189° (corr.), and has a sp. gr. 0·8866 at 14°/4°. The *picrate* melts at 163—165°, and the *methiodide* at 226—227°; the *platinichloride* melts and decomposes at 178—179°. The base unites with hydrogen chloride, forming a compound which, on reduction, yields *dimethylamino*cyclo*heptane*, $C_7H_{13}\cdot NMe_2$, which boils at 190° (corr.) and has a sp. gr. 0·8680 at 14°/4°. The *platinichloride* melts and decomposes at 190—193°, and the *methiodide* decomposes at 259°. The formation of this substance renders possible the degradation of tropidine to *cyclo*heptene, and hence its conversion into suberone.

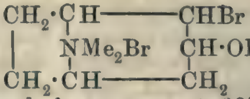
4-*Dimethylamino*cyclo*heptanol*, 
$NMe_2\cdot CH\left<\begin{array}{l}CH_2\cdot CH_2\cdot CH\cdot OH\\ CH_2\cdot CH_2\cdot CH_2\end{array}\right.$, is formed by the action of 20 per cent. sulphuric acid on Δ^4-methyltropan hydrochloride, and is a viscid oil boiling at 251° (corr.).

Δ^3-Methyltropan has previously been prepared by methylation from tropan, and is also formed by the reduction of methyltropine and by the reduction of bromotropan methobromide.

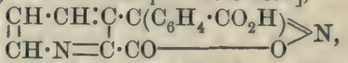
III. *Formation of Dicyclic Tropine Bases.*—Δ^4-Methyltropan readily unites with hydrogen chloride, probably forming a mixture of the *cis*- and *trans*-modifications of the hydrochloride; when this is gently heated, a portion of it, probably the *cis*-modification, undergoes an intramolecular change, which the author terms "intramolecular methylation," and is converted into tropan methochloride, which crystallises in four-sided tablets, and forms an *aurichloride* decomposing above 290°. The remainder of the hydrochloride undergoes the same change when heated at 200°.

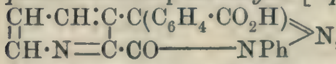
Synthesis of Tropidine.—Merling (Abstr., 1892, 358) has described the synthesis of tropidine by intramolecular change from α-methyltropidine hydrochloride, but the author was unable to obtain a pure tropidine derivative by this means. On the other hand, Δ^4-methyltropan forms a dibromide which readily changes into bromotropan methobromide, 
$\begin{array}{lll}CH_2\cdot CH & \text{——} & CHBr\\ | \quad\quad NMe_2Br & & CH_2\\ CH_2\cdot CH & \text{——} & CH_2\end{array}$, which crystallises in prisms. The *platinichloride* of the corresponding *methochloride* melts and decomposes at 246—247°. On heating with aqueous soda, this bromo-compound is converted into a tropidine derivative, from which pure tropidine can readily be obtained.

ψ-Methyltropine forms a dibromide which readily passes into the

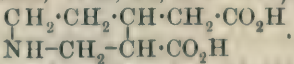
isomeric *ψ-bromotropanol methobromide,*

$$\begin{array}{llll} CH_2\cdot CH & \text{———} & CHBr & \\ | & NMe_2Br & CH\cdot OH, & \\ CH_2\cdot CH & \text{———} & CH_2 & \end{array}$$
which crystallises in small tablets and melts and decomposes at 237—238°. This compound can be prepared synthetically from α-methyltropan, the hydrogen chloride compound of which is converted by sodium carbonate into a base which has the properties of ψ-methyltropine, and behaves in a similar manner towards bromine. ψ-Bromotropanol methobromide is converted by most reducing agents into the original unsaturated base, but zinc and hydriodic acid convert it into tropidine methiodide. A. H.

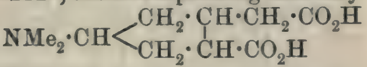
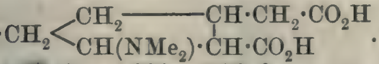
3-*p*-Toluoylpicolinic Acid and the Products of its Oxidation. By Hugo Ludwig Fulda (*Monatsh.*, 1900, 21, 981—992).—A continuation of the researches of Just (Abstr., 1898, i, 42). 3-*p*-Toluoylpicolinic acid, when oxidised with alkaline permanganate (4 mols.) yields terephthalic acid, or (with 2 mols.) 3-p-*carboxybenzoylpicolinic acid*, $CO_2H\cdot C_6H_4\cdot CO\cdot C_5NH_3\cdot CO_2H$, which crystallises with H_2O, evolves carbon dioxide at 190°, and forms a white *cadmium* salt and a *dimethyl* ester, which crystallises in long, colourless needles and melts at 110—111°; with hydroxylamine, it yields *phenylpyrid*-o-*oxazinone*-p-*carboxylic acid* [*pyridoxazinone*-p-*benzoic acid*],


$$\begin{array}{l} CH\cdot CH{:}C\cdot C(C_6H_4\cdot CO_2H) \\ CH\cdot N{=}C\cdot CO\text{————}O \end{array} > N,$$

which is obtained as a white, crystalline powder melting and decomposing at 300°; with phenylhydrazine, it yields 1-*phenyl*-3-*phenylquinolineazone*-p-*carboxylic* [7-*phenylbenzotriazin*-8-*one*-5-p-*benzoic*] *acid*,

$$\begin{array}{l} CH\cdot CH{:}C\cdot C(C_6H_4\cdot CO_2H) \\ CH\cdot N{=}C\cdot CO\text{————}NPh \end{array} > N,$$
which is obtained as a yellowish mass, does not melt below 320°, and gives a green coloration with ferric chloride and concentrated sulphuric acid. When heated to 210°, the dicarboxylic acid loses carbon dioxide and is converted into 3-*phenylpyridylketone*-p-*carboxylic acid*, $C_5NH_4\cdot CO\cdot C_6H_4\cdot CO_2H$, which crystallises in colourless, silky leaflets, melts at 267°, and forms a *hydrochloride*, which crystallises in yellowish needles, a white, amorphous *silver* salt, a *cadmium* salt, which crystallises, with H_2O, in clusters of leaflets, and a *phenylhydrazone*, which is obtained as a yellow, microcrystalline mass and melts and decomposes at 246—248°.

R. H. P.

Constitution of the Cinchona Alkaloids. VI. Conversion of Cincholeuponic Acid into an Acid Free from Nitrogen. By Zdenko H. Skraup (*Monatsh.*, 1900, 21, 879—912).—Cincholeuponic acid has the constitution

$$\begin{array}{l} CH_2\cdot CH_2\cdot CH\cdot CH_2\cdot CO_2H \\ NH{-}CH_2{-}CH\cdot CO_2H \end{array}.$$

When diethyl methylcincholeuponate methiodide (Abstr., 1897, i, 99) is treated with potassium hydroxide, it is converted into *diethyl dimethylcincholeuponate*, which is a colourless oil boiling at 167—169° under 16 mm. pressure and forms a *platinochloride*, which crystallises in glistening leaflets and melts at 211—212°; the corresponding *acid* may have the constitution represented by  $NMe_2\cdot CH<\begin{matrix} CH_2\cdot CH\cdot CH_2\cdot CO_2H \\ CH_2\cdot CH\cdot CO_2H \end{matrix}$ or  $CH_2<\begin{matrix} CH_2 \text{———} CH\cdot CH_2\cdot CO_2H \\ CH(NMe_2)\cdot CH\cdot CO_2H \end{matrix}$. It is obtained as small, white, crystals, melts at 286—287°, forms an *aurichloride*, which sinters at 192° and melts at 201—202°, and, in contradistinction to its ester, is only oxidised with difficulty, it does not combine with bromine, but forms a *hydrobromide*, which melts and decomposes at 271°; when treated with methyl iodide and potassium hydroxide, the diethyl ester is converted into *diethyl trimethylcincholeuponate iodide* which is obtained in clusters of crystals, forms a *platinichloride* which crystallises in orange-yellow laminæ and melts and decomposes at 220—222°, and an *aurichloride*, which crystallises in lustrous, thin leaflets and melts at 196°.

When dimethylcincholeuponic acid is fused with potassium hydroxide, dimethylamine, and *butane-aγ-dicarboxy-β-acetic acid*,

$$CO_2H\cdot CHMe\cdot CH(CH_2\cdot CO_2H)\cdot CH_2\cdot CO_2H,$$

are obtained; this acid crystallises in monoclinic plates, melts at 138·5—140°, forms amorphous salts, and is unattacked by hydrogen iodide; it can be synthesised by warming a mixture of diethyl methylglutaconate and diethyl sodiomalonate and hydrolysing the tetraethyl ester of butane-αγ-dicarboxy-β-malonate,

$$CO_2H\cdot CHMe\cdot CH[CH(CO_2H)_2]\cdot CH_2\cdot CO_2H,$$

which, when warmed with hydrochloric acid, evolves carbon dioxide and yields an acid corresponding in all its properties with that obtained from cincholeuponic acid. R. H. P.

Derivatives of Quinolinic and Cinchomeronic Acids. By ALFRED KIRPAL (*Monatsh.*, 1900, **21**, 957—964).—The acid esters previously described by the author (Abstr., 1900, i, 51) as β-quinolates are really the α-compounds, since, when treated with aqueous ammonia, they yield α-quinolinamic acid (Abstr., 1894, i, 301), which can be reconverted into the esters by heating them in a sealed tube with the alcohols at 100°.

Methyl α-aminonicotinate crystallises in long, white needles and melts at 85°, and when treated with aqueous ammonia yields the corresponding *amide* which crystallises in long, broad needles, melts at 195°, and can be recovered, unaltered, after heating with methyl alcohol under pressure. Monomethyl cinchomeronate (Abstr., 1889, 1016, and 1900, i, 52), when treated with aqueous ammonia, yields *cinchomeronamic acid*, which crystallises in prismatic tablets, melts at 170°, and when heated in a sealed tube with methyl alcohol at 100° is reconverted into methyl cinchomeronate. R. H. P.

Chloro- and Bromo-amino-derivatives of Diacetylphenylenediamines. By FREDERICK D. CHATTAWAY and KENNEDY J. P. ORTON (*Ber.*, 1900, **34**, 160—167. Compare Trans., 1899, **75**, 1046; 1900, **77**, 134, 789, 797, 800; Abstr., 1900, i, 151, 152; this vol., i, 23).—All three diacetylphenylenediamines, when suspended in chloroform and shaken with a solution of hypochlorous or hypobromous acid containing potassium hydrogen carbonate, yield the corresponding chloro- or bromo-amines, $C_6H_4(NXAc)_2$ [$X = Cl$ or Br]; these, when left in contact for a long period with acetic acid, change into the isomeric substituted compounds, $C_6H_2X_2(NHAc)_2$. The transformation is complete only in the case of the meta-compounds, whilst the ortho- and para-derivatives give rise simultaneously to dark-coloured, amorphous products.

o-*Diacetyldichlorodiaminobenzene*, $C_6H_4(NClAc)_2$, crystallises in colourless, lustrous, four-sided prisms and decomposes explosively at about 94°; in acetic acid solution, it is slowly converted into a *diacetyldiaminodichlorobenzene* [probably $(NHAc)_2 : Cl_2 = 1 : 2 : 4 : 5$], which crystallises from alcohol in slender needles and decomposes at 290°.

o-*Diacetyldibromodiaminobenzene* forms irregular, yellowish prisms and explodes at 76—80°; the derived *diacetyldiaminodibromobenzene* [probably $(NHAc)_2 : Br_2 = 1 : 2 : 4 : 5$] crystallises from alcohol in slender, white needles and melts and decomposes at 286°.

m-Diacetyldichlorodiaminobenzene melts at 160—161°, not at 150—151° as stated by Morgan (Trans., 1900, **77**, 1208). 4 : 6-*Dichloro*-1 : 3-*diacetyldichlorodiaminobenzene*, $C_6H_2Cl_2(NClAc)_2$, forms small, colourless prisms, melts at 127°, and decomposes at about 240°; when boiled with glacial acetic acid, it does not undergo isomeric change, but is hydrolysed to 4 : 6-dichloro-1 : 3-diacetyldiaminobenzene.

4 : 6-*Dibromo*-1 : 3-*diacetyldichlorodiaminobenzene* forms tufts of small, lustrous, colourless prisms, melts at 181°, and decomposes at 220—230°.

m-Diacetyldibromodiaminobenzene could not be prepared owing to its rapidly undergoing further change.

4 : 6-*Dibromodiacetylmonobromo*-1 : 3-*phenylenediamine*,

$$NHAc\cdot C_6H_2Br_2\cdot NBrAc,$$

is obtained as a yellow, flocculent precipitate on adding *m*-diacetyldiaminobenzene to an excess of ice-cold hypobromous acid, containing only a small quantity of potassium hydrogen carbonate; it is always impure, and melts and decomposes at 60—70°. 4 : 6-*Dibromo*-1 : 3-*diacetyldibromodiaminobenzene*, the final product of the action of hypobromous acid on *m*-diacetyldiaminobenzene, crystallises in aggregates of sulphur-yellow prisms and melts and decomposes at 172°. When boiled with glacial acetic acid, it is hydrolysed to 4 : 6-dibromo-1 : 3-diacetyldiaminobenzene, but can be recrystallised unchanged from acetic anhydride.

p-*Diacetyldichlorodiaminobenzene* crystallises in small, colourless prisms and explodes at 103°. When left with glacial acetic acid at the ordinary temperature, heat is developed, and an amorphous product formed; if, however, the solution is kept cool by ice, a small quantity of 3 : 6-dichloro-1 : 4-diacetyldiaminobenzene, melting at 301°, is formed.

3 : 6-*Dichloro*-1 : 4-*diacetyldichlorodiaminobenzene* forms short, colourless prisms, decomposes at 163°, and is only hydrolysed when heated with glacial acetic acid in a sealed tube.

p-Diacetyldiaminobenzene, with hypobromous acid, fails to yield a *p*-diacetyldibromodiaminobenzene; only a yellow, amorphous substance could be isolated which decomposed at 60°, and, apparently, was *diacetylmonobromo*-p-*phenylenediamine*, $NHAc\cdot C_6H_4\cdot NBrAc$, in a somewhat impure state.

W. A. D.

Tertiary Aromatic Amines. IV. By CARL HAEUSSERMANN (*Ber.*, 1901, **34**, 38—40).—Of the two tetraphenylphenylenediamines prepared by the action of *p*-dichlorobenzene on potassium diphenylamine (Abstr., 1899, i, 684), the '*α*,' melting at 199—200° is the para-compound; the '*β*,' melting at 127—129°, can be further purified by crystallising from toluene and then melts at 137·5—138°, and is identical with the product from *o*-dichlorobenzene (Abstr., 1900, i, 365), yielding also an identical nitro-derivative; the product of the latter reaction is thus a meta-, and not an ortho-compound as was previously supposed.

In a similar manner, it is shown that the product obtained by the action of *o*-chlorotoluene on potassium diphenylamine is identical with that from *m*-chlorotoluene, and is not a diphenyl-*o*-toluidine, as was previously supposed, but the meta-compound. T. M. L.

Condensation of Aromatic Nitroso-compounds with Methylene Derivatives. III. By FRANZ SACHS and EDUARD BRY (*Ber.*, 1901, **34**, 118—123. Compare Abstr., 1900, i, 362).—The *p*-nitroso-derivatives of the secondary bases, ethylaniline and methylaniline, react with methylene derivatives in a similar manner to the corresponding *p*-nitroso-derivatives of tertiary bases. 4-*Ethylaminophenyl-μ-cyanoazomethinephenyl*, $NHEt\cdot C_6H_4\cdot N\colon CPh\cdot CN$, is formed by the condensation of *p*-nitrosoethylaniline and benzyl cyanide in presence of sodium carbonate, and crystallises in dark red needles melting at 112°. When heated with dilute mineral acids, it yields benzoyl cyanide and ethylphenylenediamine.

4-*Ethylaminophenyl-μ-cyanoazomethine-4′-nitrophenyl*,

$$NHEt\cdot C_6H_4\cdot N\colon C(CN)\cdot C_6H_4\cdot NO_2,$$

is prepared in a similar manner from *p*-nitrobenzyl cyanide, and crystallises in silky, dichroic needles melting at 164°. 4 *Methylaminophenyl-μ-cyanoazomethinephenyl*, $NHMe\cdot C_6H_4\cdot N\colon CPh\cdot CN$, crystallises in carmine-red, silky needles melting at 126°. 4-*Methylaminophenyl-μ-cyanoazomethine-4′-nitrophenyl* forms silky, dichroic needles melting at 188°. *Ethyl 4-methylaminophenyl-μ-cyanoazomethinecarboxylate*, $NHMe\cdot C_6H_4\cdot N\colon C(CN)\cdot CO_2Et$, prepared from *p*-nitrosomethylaniline and ethyl cyanoacetate, crystallises in small, dichroic cubes melting at 136°.

4-*Diethylaminophenyl-μ-cyanoazomethine-4′-nitrophenyl hydrochloride*, $C_{18}H_{18}O_2N_4,HCl$, is an amorphous, lemon-yellow powder melting at 194°.

As previously described, the condensation products of *p*-nitroso-derivatives of tertiary aromatic bases with benzyl or nitrobenzyl cyanide, are decomposed by hydrochloric acid, forming a substituted phenylenediamine and a ketocyanide, whilst hydroxylamine hydrochloride yields the same base and the oxime of the ketone. Hydrazine hydrochloride acts in a similar manner to hydrochloric acid, whilst phenylhydrazine hydrochloride resembles hydroxylamine hydrochloride in its action. Thus the condensation product from *p*-nitrosodiethylaniline and benzyl cyanide, and the corresponding derivative of nitrosodimethylaniline, when treated with phenylhydrazine hydrochloride, both yield *benzoylcyanide phenylhydrazone*, $CPh(CN)\colon N\cdot NHPh$, which crystallises in yellow needles melting at 152°. This compound is not formed by the direct action of benzoyl cyanide on phenylhydrazine, which yields benzoylphenylhydrazine. Aniline hydrochloride acts in a similar manner, but yields, as final product, the phenylamidine corresponding with the ketocyanide. Thus the condensation product of *p*-nitrosodiethylaniline with benzyl cyanide yields diphenylbenzenylamidine, $NHPh\cdot CPh\colon NPh$, whilst that derived from *p*-nitrobenzyl cyanide yields s-*diphenyl*-p-*nitrobenzenylamidine*, $NHPh\cdot C(C_6H_4\cdot NO_2)\colon NPh$, which forms a *hydrochloride* melting at 293°, but could not itself be obtained crystalline. A. H.

A Simple Means of obtaining Secondary Symmetrical Hydrazines. By Wilhelm Autenrieth and Paul Spiess (*Ber.*, 1901, **34**, 187—189).—Secondary symmetrical acylhydrazines of the type $(R\cdot CO\cdot NH)_2$ can be readily prepared by gradually adding the corresponding acid anhydride, $(R\cdot CO)_2O$, to the calculated quantity of 50 per cent. aqueous hydrazine hydrate at 0°. s-n-*Dibutyrylhydrazine*, $N_2H_2(COPr^{\alpha})_2$, prepared from *n*-butyric anhydride, crystallises from dilute alcohol in lustrous, white leaflets and melts at 162—163°. s-*Diisovalerylhydrazine* and s-n-*hexoylhydrazine* are similar and melt at 184° and 159° respectively. *s*-Dibenzoylhydrazine was also prepared by this method from benzoic anhydride. W. A. D.

Derivatives of Ethyl Phenylhydrazonecyanoacetate. By W. Lax (*J. pr. Chem.*, 1901, [ii], **63**, 1—29).—Krückeberg (Abstr., 1894, i, 369) has shown that the condensation products of ethyl cyanoacetate with diazonium salts exist in two isomeric modifications; when the alkaline solution of the ester is treated with carbon dioxide, the stable β-modification separates, whilst by the action of hydrochloric acid, the labile α-modification is produced. The object of the present investigation was to determine whether these substances should be regarded as azo- or hydrazone-compounds.

The β-modification of *ethyl* p-*methoxyphenylhydrazonecyanoacetate*, $OMe\cdot C_6H_4\cdot NH\cdot N\colon C(CN)\cdot CO_2Et$, obtained by the action of ethyl cyanoacetate on a diazotised solution of *p*-anisidine, crystallises in long, silky, yellow needles, melts at 85°, and dissolves readily in alcohol, ether, or benzene. The α-modification melts at 116—118°, and by repeated crystallisation from alcohol is converted into the β-modification. The *sodium* and *silver* salts of the ester are described. When an aqueous solution of the sodium salt is treated with carbonyl chloride, condensation does not occur, but the β-modification of the ester is produced. The solubility of the α-modification in benzene at 20° is 3·87 per cent., whilst that of the β-form is 7·33 per cent.

The β-modification of *ethyl* o-*methoxyphenylhydrazonecyanoacetate* crystallises in long needles and melts at 145°. When an alkaline solution of the ester is treated with hydrochloric acid, hydrolysis occurs with formation of the corresponding *acid*, melting at 175—176°. The α-modification, obtained by treating the *sodium* salt of the ester with dilute acetic acid, crystallises from ether and melts at 108°. An attempt to prepare a third modification by the action of carbon dioxide on a solution of the sodium salt at 70—80° (compare Weissbach, Abstr., 1898, i, 366) resulted in the production of a red compound accompanied by the β-modification from which it could not be separated.

The *ammonium* and *silver* salts of the ester are described. The solubility of the α-compound in benzene at 18° is 12·09 per cent., whilst that of the β-form is 3·24 per cent.

The β-modification of *ethyl* p-*ethoxyphenylhydrazonecyanoacetate*, $OEt\cdot C_6H_4\cdot NH\cdot N\colon C(CN)\cdot CO_2Et$, crystallises from alcohol in large, lustrous plates, and melts at 98°. The α-compound melts at 133—134°; its solubility in benzene at 20° is 2·51 per cent., whilst that of the β-form is 38·43 per cent.

The β-modification of *methyl ethyl carboxyphenylhydrazonecyanoacetate*, $CO_2Me\cdot C_6H_4\cdot NH\cdot N\colon C(CN)\cdot CO_2Et$, obtained by the action of ethyl cyanoacetate on diazotised methyl anthranilate, crystallises in small, yellow needles, melts at 155°, and is easily soluble in alcohol or ether. The α-modification melts at 139—140°. When the alkaline solution of the ester is heated, hydrolysis occurs, and on addition of hydrochloric acid, a yellow *acid*, $CO_2H\cdot C_6H_4\cdot NH\cdot N\colon C(CN)\cdot CO_2H$, is obtained; its *silver* salt was prepared.

By the action of ethyl cyanoacetate (1 mol.) on a diazotised solution of benzidine (1 mol.), a dark brown condensation *product*,

$$CO_2Et\cdot C(CN)\colon N\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot N_2\cdot Cl,$$

is obtained which unites with β-naphthol to form *ethyl β-naphtholazodiphenylhydrazonecyanoacetate*.

The *β-modification* of ethyl diphenyldihydrazonecyanoacetate (Favrel, Abstr., 1899, i, 58) melts at 208°. By the action of sodium hydroxide on the ester, *tetrasodium* diphenyldihydrazonecyanoacetate,

$$C_{12}H_8[NNa\cdot N\colon C(CN)\cdot CO_2Na]_2,$$

is produced; the corresponding *silver* salt and the *acid* were prepared, but the latter could not be obtained pure. The *α-modification*, obtained by the action of dilute hydrochloric acid on the *disodium* salt of the ester, melts at 233°.

The *β-modification* of ethyl di-*o*-tolyldihydrazonecyanoacetate (Favrel, *loc. cit.*), prepared from the *sodium* salt of the ester, melts at 222°; the *α-modification* melts at 174—175°, and is thereby converted into the β-form. If the sodium salt is treated with excess of hydrochloric acid, the *monoethyl* ester is produced.

Ethyl dimethoxydiphenyldihydrazonecyanoacetate, obtained by the action of ethyl cyanoacetate on a diazotised solution of dianisidine, yields an α-modification melting at 175—176°, and a β-modification melting at 273—274°; when the former is heated above its melting point, it is converted into the latter.

Ethyl p-*hydroxycarboxyphenylhydrazonecyanoacetate*, prepared by the condensation of diazotised *p*-aminosalicylic acid with ethyl cyanoacetate, could not be obtained in two modifications.

When an aqueous solution of the potassium derivative of *p*-nitrophenylnitrosoamine is added to an alcoholic solution of ethyl cyanoacetate, ethyl *p*-nitrophenylhydrazonecyanoacetate is obtained identical with that prepared by Uhlmann (Abstr., 1895, i, 274) by the action of ethyl cyanoacetate on *p*-nitrodiazobenzene chloride; the α-modification melts at 177°, and the β-form at 191—192°. It follows, therefore, that the condensation products of ethyl cyanoacetate and diazobenzene salts must be regarded as hydrazone compounds.

Condensation products of benzidine and ethyl cyanoacetate with phenol, resorcinol, α- and β-naphthol, and 2 : 7-dihydroxynaphthalene, and also those of *o*-tolidine and ethyl cyanoacetate, and of dianisidine and ethyl cyanoacetate with the same phenols have been prepared and their tinctorial properties examined. E. G.

New Condensation of Ethyl Diazoacetate. By EDUARD BUCHNER and C. VON DER HEIDE (*Ber.*, 1901, **34**, 345—348).—*Ethyl pyrazoline*-3 : 4 : 5-*tricarboxylate*, $C_3N_2H_3(CO_2Et)_3$, is prepared by heating ethyl diazoacetate on the water-bath either alone or in the presence of ethyl *gem*-dimethylacrylate ; it crystallises from alcohol in colourless needles and melts at 98—99°.

Ethyl pyrazole-3 : 4 : 5-*tricarboxylate*, $C_3N_2H(CO_2Et)_3,2H_2O$, obtained by treating the preceding compound with 1 mol. of bromine dissolved in chloroform, crystallises from boiling water in colourless prisms and melts at 71°. The substance loses its water of crystallisation when kept in a vacuum over sulphuric acid, and the melting point rises to 91° ; it is stable towards alkaline permanganate solution, whilst the preceding ester rapidly decolorises this reagent.

Pyrazole-3 : 4 : 5-tricarboxylic acid, $C_3N_2H(CO_2H)_3$, is produced by hydrolysing its ester with dilute sulphuric acid ; it yields pyrazole when heated at 230—240°. The yield of pyrazole from ethyl diazoacetate is sufficiently good to warrant the use of this condensation in the preparation of the base. G. T. M.

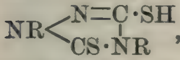
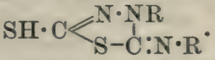
Action of Phenylhydrazine on Aldol and on Crotonaldehyde. By GIOVANNI BATTISTA TRENER (*Monatsh.*, 1900, **21**, 1111—1121).—A 40—50 per cent. yield of 1-phenyl-5-methyl pyrazoline (Abstr., 1893, i, 229) is obtained when freshly prepared aldol is treated with phenylhydrazine at the ordinary temperature. Phenylhydrazine and crotonaldehyde yield the same product. If care is taken to avoid rise in temperature and the reacting substances are left in contact for 5 weeks, a polymeride, $(C_{10}H_{12}N_2)_n$, melting at 157° is formed. It is a yellow powder insoluble in alcohol or ether, and when distilled under 18 mm. pressure is reconverted into the phenylmethylpyrazoline.

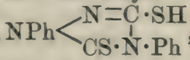
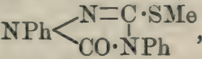
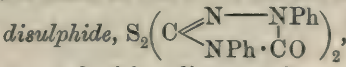
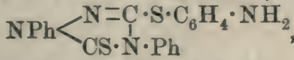
1-*Phenyl*-5-*methylpyrazoline dibromide*, $C_{10}H_{12}N_2Br_2$, forms colourless crystals melting at 198°, and readily turns red on exposure to light. The *ethiodide*, $C_{10}H_{12}N_2,2EtI$, may be obtained crystalline after several weeks ; it is insoluble in chloroform and decomposes at 230° without melting. The *hydrochloride*, $C_{10}H_{12}N_2,2HCl$, forms colourless, glistening plates but the yield is very poor.

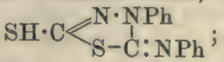
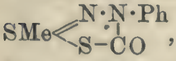
A *compound*, $C_{17}H_{16}N_2$, is obtained when benzaldehyde and phenylmethylpyrazoline are gently warmed for 2—3 hours ; it crystallises in long, yellow prisms, melts at 140°, and is insoluble in water or acetic acid. J. J. S.

Absorption Spectra of Indophenols : Law of Auxochromic Groups containing Tertiary Nitrogen. By PAUL LEMOULT (*Compt. rend.*, 1901, **132**, 142—145).—The alcoholic solutions of the indophenols derived from *p*-phenylenediamine and the phenols, and containing a primary nitrogen atom in the auxochromic group, have absorption spectra showing a brilliant red band of unabsorbed light, whilst those derived from *p*-aminodimethylaniline exhibit a less pronounced red band quite distinct in position from the first. This observation is quite opposed to that of Camichel and Bayrac, who endeavour to demonstrate the fixity of the red band for all indophenols (compare this vol., i, 100). The band is fixed only when the colouring matters concerned contain the same auxochromic group, and differ only in the substituent radicles not involved in the chromophore; it is, however, very appreciably displaced on varying the radicles attached to the auxochromic nitrogen.

G. T. M.

Action of Thiocarbimides on Dithiocarbazinic Acids. By MAX BUSCH and E. WOLPERT [and in part GUSTAV OBERMILLER] (*Ber.*, 1901, **34**, 304—320. Compare Abstr., 1899, i, 825).—Dithiocarbazinic acids condense with thiocarbimides to form either triazolethiols,  $NR<\begin{array}{l}N{=}C\cdot SH\\ CS\cdot NR\end{array}$, or thiodiazolethiols,  $SH\cdot C<\begin{array}{l}N\cdot NR\\ S{-}C{:}N\cdot R\end{array}$.

Potassium phenyldithiocarbazinate condenses with phenylthiocarbimide in alcoholic solution in the presence of sodium hydroxide to form 1:4-*diphenyl*-5-*thio*-1:2:4-*triazolone*-3-*thiol*,  $NPh<\begin{array}{l}N{=}C\cdot SH\\ CS\cdot N\cdot Ph\end{array}$, which crystallises in clusters of pale yellow needles, melts at 177—178°, and when treated with potassium hydroxide and methyl iodide yields the methyl ether, 1:4-*diphenyl*-5-*thio*-1:2:4-*triazolone*-3-*thiomethane*, which can be obtained in two physical modifications melting at 120° and 125° respectively. The ether, when treated with mercuric oxide, is converted into 1:4-*diphenyltriazolone*-3-*thiomethane*,  $NPh<\begin{array}{l}N{=}C\cdot SMe\\ CO\cdot NPh\end{array}$, which crystallises in quadratic prisms and melts at 103°. When the thiol is treated with mercuric oxide, the *disulphide*,  $S_2\left(C<\begin{array}{l}N{-}NPh\\ NPh\cdot CO\end{array}\right)_2$, is obtained; it melts at 227° and when treated with sodium amalgam yields 1:4-*diphenyltriazolone*-3-*thiol*, which crystallises from alcohol and melts at 135°. The thio-thiol, when oxidised with potassium permanganate, forms 1:4-*diphenyl*-5-*thio*-1:2:4-*triazolone*-3-*sulphonic acid*, $C_{14}H_{10}N_3S\cdot SO_3H$, which crystallises in small needles and melts at 343°, and with milder oxidising agents, such as iodine or ferric chloride, yields the *disulphide*, $S_2(C_{14}H_{10}N_3S)_2$, which crystallises in small, yellow needles melting at 147—148°. When treated with alcoholic ammonia, the disulphide yields ammonium mercaptide and *diphenylthiotriazolonylhydrothiamine*, $C_{14}H_{10}N_3S\cdot SNH_2$, which crystallises in yellowish needles melting at 130°; when treated with aniline, it forms *diphenyltriazolonethioaminobenzene*,  $NPh<\begin{array}{l}N{=}C\cdot S\cdot C_6H_4\cdot NH_2\\ CS\cdot N\cdot Ph\end{array}$, which crystallises in yellowish needles, melts at 175°, and forms a crystalline *hydrochloride* which is decomposed by water; and when treated with ethylaniline it yields *diphenyltriazolonethioethylaminobenzene*, $C_{14}H_{10}N_3S\cdot S\cdot C_6H_4\cdot NHEt$, which melts at 182°, and forms a *nitrosoamine* crystallising in long, yellowish needles and melting at 127°; the disulphide can also be diazotised and coupled with β-naphthol to form an *azo*-dye which crystallises in orange-red needles and melts at 243°.

When potassium phenylthiocarbazinate is heated alone with phenylthiocarbimide, a mass is obtained which, when acidified, yields *phenylthiodiazoloneanilthiol*,  $SH\cdot C{<}\begin{matrix}N\cdot NPh\\ S-C:NPh\end{matrix}$; this crystallises in leaflets, melts at 171—172°, and, when oxidised with ferric chloride, yields a *disulphide* which crystallises in yellow needles and melts at 106—107°. The thiol also forms a *methyl* ether which crystallises in prismatic plates, melts at 67°, and yields a crystalline *platinichloride*; the methyl ether, when heated with hydrochloric acid, yields *phenylthiodiazolonethiomethane*,  $SMe{<}\begin{matrix}N\cdot N\cdot Ph\\ S-CO\end{matrix}$, which crystallises in needles and can be synthesised from methyl phenyldithiocarbazinate and carbonyl chloride.

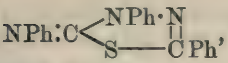
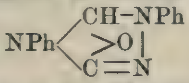
The analogous *p*-tolyl and *a*-naphthyl compounds have been prepared in a similar manner. 1-p-*Tolyl*-4-*phenyl*-5-*thiotriazolone*-3-*thiol* from potassium *p*-tolyldithiocarbazinate crystallises in needles, melts at 162—163°, forms a crystalline *sodium* salt and a *methyl* ether which crystallises in lustrous needles and melts at 153°, and, when oxidised, yields a *disulphide* which crystallises in yellow needles and melts at 205°. p-*Tolylthiodiazoloneanilthiol* crystallises in lustrous, yellow leaflets melting at 162—163°, when oxidised yields a *disulphide* which crystallises in lustrous, yellow needles and melts at 130°, and forms a *methyl* ether which crystallises in six-sided prisms, softens at 66°, and melts at 68°. p-*Tolylthiodiazolonethiomethane* crystallises in colourless needles and melts at 52°. 1-*Phenyl*-4-*tolyl*-5-*thio*-1 : 2 : 4-*triazolone*-3-*thiol*, from *p*-tolylthiocarbimide and potassium phenyldithiocarbazinate, crystallises in small, lustrous, yellow needles, melts at 178°, and forms a *methyl* ether which crystallises in lustrous leaflets and melts at 152°. *Phenylthiodiazolone*-p-*tolylthiomethane* crystallises in small tablets and melts at 101°.

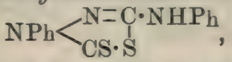
4-*Phenyl*-1-*a*-*naphthylthiotriazolonethiol*, from phenylthiocarbimide and potassium *a*-naphthyldithiocarbazinate, is obtained in aggregates of crystals melting at 120°, and forms a *methyl* ether which crystallises in needles and melts at 197—198°.

Phenylcarbimide and methyl phenyldithiocarbazinate condense to form *methyl* 2 : 4-*diphenylsemicarbazide*-1-*dithiocarboxylate*,

$$NHPh\cdot CO\cdot NPh\cdot NH\cdot CS_2Me,$$

which crystallises in white needles and melts at 186°. R. H. P.

Isomeric Thiosemicarbazides. By MAX BUSCH and HERM. HOLZMANN (*Ber.*, 1901, **34**, 320—345).—The thiosemicarbazides described by Marckwald (Abstr., 1893, i, 46) are shown to be, not physical isomerides, but structural isomerides of the types $NH_2\cdot NR\cdot CS\cdot NHR$ and $NHR\cdot NH\cdot CS\cdot NHR$, so that the compound described by Marckwald as *a*-diphenylthiosemicarbazide is *βδ*-diphenylthiosemicarbazide and the *β*-compound is *aδ*-diphenylthiosemicarbazide. When treated with nitrous acid, the *βδ*-compound is converted into thiocarbanilide, and the *aδ*-compound into an azonitroso-compound, which is to be described later. When the *βδ*-compound is treated with benzaldehyde, it condenses to form *benzylidene-βδ-diphenylthiosemicarbazide*, which crystallises in yellowish needles, melts at 167—168°, decomposes at 220°, forms a crystalline *potassium* salt which sinters at (about) 180°, and a *methyl* derivative which crystallises in needles and melts at 127—128° and, when oxidised with ferric chloride, yields *diphenylthiodiazoloneanil*,  $NPh{:}C<\begin{matrix}NPh\cdot N\\ S\text{———}CPh\end{matrix}$, which crystallises in lustrous, silky needles melting at 184—185°. When the αδ-compound is treated with benzaldehyde, a *compound*, $C_{20}H_{15}N_3S$, is obtained; this forms a *methiodide*, which, when treated with alcoholic potash, yields a basic *compound*, which crystallises in leaflets and melts at 152°. The authors ascribe the formula  $NPh<\begin{matrix}CH-NPh\\ >O\ |\\ C=N\end{matrix}$ to the compound obtained by Marckwald (*loc. cit.*) after oxidation with hydrogen peroxide of the substance formed by the action of carbonyl chloride on the βδ-compound. When treated with thiocarbonyl chloride, the βδ-compound yields phenylthiodiazoloneanilthiol (see preceding abstract), while the αδ-compound yields *phenylanilinodithiodiazolone*,



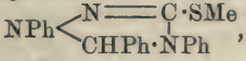
$$NPh<\begin{matrix}N{=}C\cdot NHPh\\ CS\cdot S\end{matrix},$$

which crystallises in needles and melts at 188—189°.

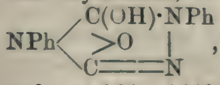
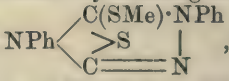
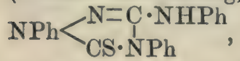
Both compounds, when treated with methyl iodide and potassium hydroxide, yield methyl ethers; the *methyl* ether of the βδ-compound (afterwards named the α-methyl ether), $NH_2\cdot NPh\cdot C(SMe){:}NPh$, crystallises in lustrous needles, melts at 77—78°, and forms a *platinichloride* which crystallises in leaflets and decomposes at 155°, the *methyl* ether of the αδ-compound (afterwards named the β-methyl ether), $NHPh\cdot NH\cdot C(SMe){:}NPh$, crystallises in stout needles, softens at 77°, and melts at 80°. When treated with nitrous acid, the α-ether yields the methyl ether of thiocarbanilide, whilst the β-ether yields *benzeneazophenyliminomethane-thiomethane*, $NPh{:}N\cdot C(SMe){:}NPh$, which crystallises in lustrous, dark-red needles and melts at 66°. With benzenesulphonic chloride, the α-ether yields the *sulphone*,

$$SO_2Ph\cdot NH\cdot NPh\cdot C(SMe){:}NPh,$$

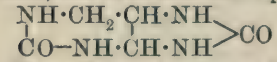
which forms rhombic crystals soluble in alkalis and melts at 116—118°, and the β-ether yields the *sulphone*, $SO_2Ph\cdot NPh\cdot NH\cdot C(SMe){:}NPh$, which is insoluble in alkalis, crystallises in leaflets, and melts at 146—147°. Carbon disulphide combines with the α-ether forming the corresponding *dithiocarbazinic acid*, $CS_2H\cdot NH\cdot NPh\cdot C(SMe){:}NPh$, which is obtained as a yellow, crystalline powder melting at 174°. Benzaldehyde condenses with the α-ether, giving a product identical with the ether of the benzylidene compound previously mentioned, and with the β-ether to form 1 : 4 : 5-*triphenyldihydro*-1 : 2 : 4-*triazole-3-thiomethane*,



$$NPh<\begin{matrix}N{=\!=}C\cdot SMe\\ CHPh\cdot NPh\end{matrix},$$

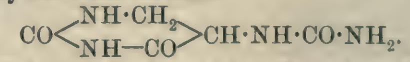
which crystallises in six-sided tablets and melts at 108—109°. The ether of the base obtained by Marckwald by the action of carbonyl chloride on the βδ-compound (*loc. cit.*) can also be obtained by the action of carbonyl chloride on the α-ether; when treated with potassium hydroxide, it yields the corresponding hydroxyl *compound*,  $NPh<\begin{matrix}C(OH)\cdot NPh\\ >O\ \ |\\ C{=\!=}N\end{matrix}$, which crystallises in lustrous, flat needles, and melts at 161—162°. Carbonyl chloride reacts with the β-ether, forming 1 : 4-diphenyltriazolone-3-thiomethane (see preceding abstract). The corresponding thio-compounds are obtained by treating the ethers with thiocarbonyl chloride; the *compound*,  $NPh<\begin{matrix}C(SMe)\cdot NPh\\ >S \quad | \\ C{=\!=\!=}N\end{matrix}$, crystallises in short, grey needles, and melts at 156—157°. When the ethers are warmed with acetic anhydride, the α-ether is converted into phenylmethyloxydiazoline (Freund and König, Abstr., 1894, i, 96), but the β-ether forms an *acetyl* derivative, which crystallises in white needles and melts at 139—140°. When treated with phenylthiocarbimide, the α-ether yields phenylanilinothiodiazoloneanil (Freund and König, *loc. cit.*), but the β-ether yields the *compound*  $NPh<\begin{matrix}N{=}C\cdot NHPh\\ | \\ CS\cdot NPh\end{matrix}$, which crystallises in colourless, silky needles, melts at 179°, and when treated with methyl iodide yields a methyl derivative melting at 112—113°. R. H. P.

Products of the Reduction of Uric Acid. By Julius Tafel (*Ber.*, 1901, **34**, 258—278).—Uric acid was reduced electrolytically in sulphuric acid solution between prepared lead electrodes (Abstr., 1900, ii, 588). The uric acid must be pure, as mere traces of certain metals (platinum and mercury, for instance, but not iron) hinder the reaction greatly. Moreover, in order that crystalline products may be obtained, it is necessary that the temperature should be kept low; this is effected by immersing the lead beaker, which serves as cathode, in ice-cold water or in a freezing mixture, whilst a current of ice-cold water, or of salt solution cooled below 0°, is passed through the hollow anode. In general, unless the conditions are specially adjusted, three products are obtained, purone, *iso*purone, and tetrahydrouric acid; of these, the first and third probably have the formulæ



$$\begin{matrix}NH\cdot CH_2\cdot CH\cdot NH\\ CO-NH\cdot CH\cdot NH\end{matrix}>CO$$

and

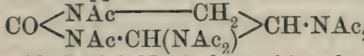


$$CO<\begin{matrix}NH\cdot CH_2\\ NH-CO\end{matrix}>CH\cdot NH\cdot CO\cdot NH_2.$$

Some determinations of the solubility of uric acid in sulphuric acid of various strengths are given in the paper.

Purone, $C_5H_8O_2N_4$, is best obtained by electrolysing a 10 per cent. solution of uric acid in 75 per cent. sulphuric acid at 5—8° with a current concentration of 120 amperes, freeing the solution from sulphuric acid, concentrating it under diminished pressure, and recrystallising the product from water. It decomposes rather above 250° when heated; it has practically no basic properties; it does not dissolve in cold dilute alkalis more than in water, but heating with alkalis converts it into *iso*purone; it does not decolorise permanganate or bromine water; it gives no coloration with ferric chloride; when heated with acetic anhydride, it yields eventually the same product as *iso*purone does; when heated with acids, it appears first to form *iso*purone, but eventually forms other products; when heated at 150° with aqueous barium hydroxide, it loses 2 mols. of carbon dioxide, but yields no product that could be obtained crystalline; no well characterised product could be obtained by oxidising it with nitric acid or with chlorate and hydrochloric acid.

iso*Purone*, $C_5H_8O_2N_4$, is best obtained by heating purone with five times its weight of 10 per cent. aqueous sodium hydroxide, previously heated to 100°, for 10 minutes at that temperature. It decomposes at 240°, appears to crystallise in two forms differing in their solubility in water, decolorises permanganate and bromine water, and gives a brownish-violet coloration with ferric chloride; it hardly dissolves in cold water, but dissolves in not too dilute alkali hydroxides, although not in alkali carbonates or in ammonia; a *nitrate*, with $1HNO_3$, and *picrate* were prepared, and the former was analysed. When boiled with acetic anhydride, it forms first a *triacetyl* derivative melting at 197°, and eventually loses carbon dioxide and forms a *substance* melting at 154—159°, which appears to have the constitution



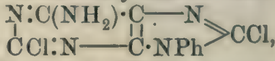
$$CO<\begin{matrix}NAc\text{———}CH_2\\NAc\cdot CH(NAc_2)\end{matrix}>CH\cdot NAc_2.$$

Tetrahydrouric acid, $C_5H_8O_3N_4$, is formed in relatively larger amount when stronger acid and a low current density are employed, namely, 80 per cent. acid and a current of 15 amperes; the temperature could not then be kept lower than 20—24°. It melts and decomposes at 212—213°, does not decolorise permanganate or bromine water, is feebly acid to litmus, and dissolves in aqueous sodium hydroxide, and also in aqueous sodium carbonate or ammonia. When boiled with aqueous barium hydroxide, it loses about 1 mol. of carbon dioxide, and when heated with acids, it loses carbon dioxide and ammonia, but in neither case could crystalline products be isolated. When tetrahydrouric acid is dissolved in aqueous barium hydroxide, barium nitrite added, the mixture dropped slowly into hot dilute sulphuric acid, barium nitrate added, and the rest of the sulphuric acid removed with barium hydroxide, the filtered solution yields, when concentrated, the *nitrate* of an unstable *base*, $C_4H_7O_2N_3,HNO_3$; this salt decomposes at 270—290°; the *sulphate*, *picrate*, and *platinichloride*, with $2H_2O$, of the base were prepared, and the last of these was analysed. Although the nitrate is not acted on further by nitrous acid in acid solution, when it is added to a strong solution of barium nitrite, it reacts with one equivalent of the latter, and two crystalline products are formed which melt respectively at 170—180° and 238°. C. F. B.

Products of the Reduction of Methylated Uric Acids. By Julius Tafel (*Ber.*, 1901, 34, 279—291).—Various methyluric acids were reduced electrolytically to the corresponding purones by much the same method as was employed in the case of uric acid itself (preceding abstract), except that rather weaker acid was usually employed (50—70 per cent.), and, in the case of the tri- and tetra-methyl compounds, a lower current concentration (10—15 amperes). The formation of an *iso*purone in addition to a purone appears to be general; on the other hand, a compound corresponding to tetrahydrouric acid was not obtained in any case. Tetramethylpurone, however, was not accompanied by any *iso*purone, nor is it converted into an *iso*purone by treatment with an alkali; in this compound, of course, all the imino-hydrogen atoms are replaced by methyl groups. Both δ- and ζ-4-methyluric acid appear to yield the same 4-methylpurone, although the δ-product, as actually obtained, was rather less soluble in cold water than the other.

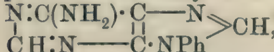
4-*Methylpurone*, $C_6H_{10}O_2N_4$, decomposes rather above 260°; 4-*methyl*iso*purone*, $C_6H_{10}O_2N_4,2H_2O$, was also obtained in small quantity. 4 : 6-*Dimethylpurone*, $C_7H_{12}O_2N_4$, melts and decomposes at about 240°; the 3 : 4- and 1 : 3-isomerides were also obtained in the crystalline state. 1 : 4 : 6-*Trimethylpurone*, $C_8H_{14}O_2N_4$, melts at 209°, loses 1 mol. of carbon dioxide when boiled with aqueous barium hydroxide, does not form salts with mineral acids, but forms a *picrate*, with $1C_6H_3O_7N_3$, and a *monoacetyl* derivative melting at 128·5° and 184° respectively; when heated with 10 per cent. aqueous sodium hydroxide at 100°, it is converted into 1 : 4 : 6-*trimethyl*iso*purone*, which melts at 211—212°, and gives a brownish-violet coloration with ferric chloride. *Tetramethylpurone*, $C_9H_{16}O_2N_4$, melts at 170°, loses 2 mols. of carbon dioxide when boiled with aqueous barium hydroxide, and is not converted into an *iso*purone by alkalis. C. F. B.

3-Phenyladenine. By ERNEST FOURNEAU (*Ber.*, 1901, **34**, 112—118).—Trichloro-3-phenylpurine when treated with ammonia yields as chief product 2:5-dichloro-7-amino-3-phenylpurine,



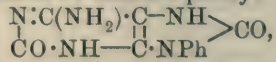
$\begin{array}{l}N{:}C(NH_2)\cdot C—N\\ CCl{:}N—C\cdot NPh\end{array}{>}CCl$,

which forms lustrous prisms melting at 265° (corr.). This is accompanied by an isomeric *substance* melting at about 327° and a *chlorodiaminophenylpurine*, $C_{11}H_9N_6Cl$, which decomposes at about 290°. These two substances are only formed in very small quantity and have not been further investigated. 2 : 5-Dichloro-7-amino-3-phenylpurine is readily reduced by hydriodic acid to 3-*phenyladenine*,



$\begin{array}{l}N{:}C(NH_2)\cdot C—N\\ CH{:}N—C\cdot NPh\end{array}{>}CH$,

which crystallises in lustrous tablets melting at 245—246° (corr.) and sublimes when further heated. The *hydrochloride*, *aurichloride*, and *platinichloride* all crystallise well. Hydrochloric acid at 130° converts 2 : 5-dichloro-7-amino-3-phenylpurine into 7-*amino*-2 : 5-*dioxy*-3-*phenylpurine*,

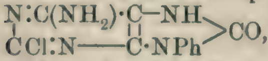


$\begin{array}{l}N{:}C(NH_2)\cdot C—NH\\ CO\cdot NH—C\cdot NPh\end{array}{>}CO$,

which crystallises in colourless needles and decomposes above 285°. The *hydrochloride*, *aurichloride*, and *platinichloride* are all crystalline.

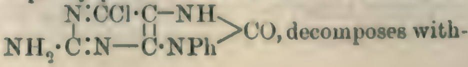
The base does not yield guanidine on oxidation with chlorine, and since it can also be obtained from the product of the action of ammonia on 5 : 7-dichloro-2-oxy-3-phenylpurine, it must have the constitution already given, from which that of 3-phenyladenine follows.

5 : 7-Dichloro-2-oxy-3-phenylpurine is converted by ammonia into a mixture of two compounds. 5-*Chloro*-7-*amino*-2-*oxy*-3-*phenylpurine*,



$\begin{array}{l}N{:}C(NH_2)\cdot C—NH\\ CCl{:}N—C\cdot NPh\end{array}{>}CO$,

crystallises in slender needles which are moderately soluble in hot 20 per cent. hydrochloric acid and decompose without melting at about 345°. It is converted by phosphorus oxychloride into 2 : 5-dichloro-7-amino-3-phenylpurine, and by hydrochloric acid into 7-amino-2 : 5-dioxy-3-phenylpurine. The isomeric 7-*chloro*-5-*amino*-2-*oxy*-3-*phenylpurine*,



$\begin{array}{l}N{:}CCl\cdot C—NH\\ NH_2\cdot C{:}N—C\cdot NPh\end{array}{>}CO$,

decomposes without melting at about 350°, and is much less soluble in hydrochloric acid than its isomeride. A. H.

Azo-dyes from β-Naphthol and the Monosulphonic Acids of α-Naphthylamine. By GEORG VON GEORGIEVICS (*Monatsh.*, 1900, **21**, 831—844).—A comparison of the properties of the seven azo-dyes obtained by coupling β-naphthol with the monosulphonic acids of α-naphthylamine. The *dye* from 1-naphthylamine-2-sulphonic acid crystallises in glistening needles with a greenish, metallic lustre, has a solubility of 0·14 part in 100 parts of boiling water, and gives a red coloration with ferric chloride. The *dye* from 1-naphthylamine-3-sulphonic acid crystallises in clusters of dark-coloured needles, has a solubility of 0·4 to 0·7 part in 100 parts of boiling water, and gives in dilute solution a violet coloration with ferric chloride. The well-known "Echtroth A" dye from 1-naphthylamine-4-sulphonic acid has a solubility of 2·6 parts in 100 parts of boiling water and gives a yellow coloration with ferric chloride. The *dye* from 1-naphthylamine-5-sulphonic acid is very similar to "Echtroth A," and has a solubility of 13 parts in 100 parts of boiling water. The *dye* from 1-naphthylamine-6-sulphonic acid crystallises in lustrous, copper-red leaflets, has a solubility of 0·5 part in 100 parts of boiling water and in dilute solution is decolorised by ferric chloride. The *dye* from 1-naphthylamine-7-sulphonic acid crystallises in lustrous, golden needles, and in dilute solution gives a red precipitate with ferric chloride. The *dye* from 1-naphthylamine-8-sulphonic acid forms lustrous, dark brown, microscopic prisms, is very similar to the dye from the 1 : 2-acid, has a solubility of 0·21 part in 100 parts of boiling water, and in dilute solution gives a greenish-yellow coloration with ferric chloride. These dyes further give characteristic colorations with concentrated sulphuric acid, are soluble in ethyl alcohol, slightly so in amyl alcohol, and insoluble in benzene.

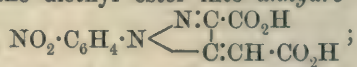
The paper concludes with a description by EDUARD VALENTA of the absorption spectra of the dyes in alcoholic solution. R. H. P.

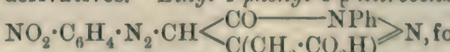
Behaviour of the Dyes obtained from the Sulphonic Acids of α-Naphthylamine and α-Naphthol with Sheep's Wool. By GEORG VON GEORGIEVICS and L. SPRINGER (*Monatsh.*, 1900, **21**, 845—851).—A comparison of the colouring properties of the dyes described in the preceding abstract. The dyes are not taken up from their aqueous solutions by the wool until after the addition of acetic acid, in which they are less soluble than in water. There is no connection between the solubility of the dye and the affinity of the wool for the latter. It is probable that the dyeing of wool with these dyes does not depend on the formation of a chemical compound between the sulphonic acid and the keratin of the wool. R. H. P.

Compounds of Ethyl Acetonedicarboxylate with Diazo-compounds and their Decomposition Products. By CARL BÜLOW and WILHELM HÖPFNER (*Ber.*, 1901, **34**, 71—90. Compare von Pechmann and Jenisch, Abstr., 1892, 161, 162; von Pechmann, 1893, i, 82, 84; Bamberger, 1892, 162; 1893, i, 84, 156; Bülow and Schlesinger, 1900, i, 56; Bülow, 1899, i, 271, 355; 1900, i, 65).—*Ethyl* p-*nitrobenzeneazoacetonedicarboxylate*,

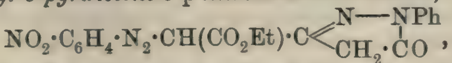
$$NO_2\cdot C_6H_4\cdot N_2\cdot CH(CO_2Et)\cdot CO\cdot CH_2\cdot CO_2Et,$$

is obtained by the action of normal diazo-derivatives of *p*-nitraniline on an acetic acid solution of the ester or of the *iso*diazo-compounds on neutral or alkaline solutions of the esters. It forms long, yellow crystals melting at 110°, and is readily soluble in most solvents, with the exception of water; it dissolves in dilute alkalis, and may be reprecipitated by the aid of carbon dioxide, but if left too long in contact with the alkali, it is hydrolysed to a wine-red solution of *trisodium* p-*nitrobenzeneazoacetonedicarboxylate*, which, on treatment with acetic acid, yields the yellowish-white *monosodium* salt. When the ester is boiled for 3 days with water, it yields ethyl *p*-nitroazobenzeneacetoacetate (Abstr., 1897, i, 616; 1899, i, 271). 1-*Nitrophenyl*-3-*methyl*-4-*benzeneazo*-5 *pyrazolone*, obtained by the action of *p*-nitrophenylhydrazine on ethyl benzeneazoacetoacetate, crystallises in yellow needles melting at 249°, and is only sparingly soluble in the usual solvents.

1-*p*-Nitrophenyl-3-methyl-4-*p*-nitrobenzeneazo-5-pyrazolone (Abstr., 1899, i, 272) and a small amount of *p*-nitrobenzeneazoacetoacetic acid are formed when the diethyl ester is hydrolysed for several days with 10 per cent. hydrochloric acid; the constitution of the dinitropyrazolone derivative thus obtained has been established by direct synthesis. Alkaline hydrolysing agents convert the diethyl ester into *anhydro*-p-*nitrobenzeneazoacetonedicarboxylate*,  $NO_2\cdot C_6H_4\cdot N\left<\begin{array}{l} N{:}C\cdot CO_2H \\ \quad\;\; C{:}CH\cdot CO_2H \end{array}\right.$; this crystallises from hot water in long, colourless needles melting at 251°, and is only sparingly soluble in ether, acetone, benzene, or light petroleum. When titrated with alkalis in the presence of phenolphthalein, it gives numbers indicating the presence of two carboxylic groups. The *ammonium hydrogen* salt forms colourless crystals melting at 275° and is readily soluble in water; its aqueous solution gives precipitates with the soluble salts of most of the heavy metals. The *monoethyl* ester, obtained by the action of dry hydrogen chloride on an alcoholic solution of the acid, crystallises in colourless needles melting at 180°; it is almost insoluble in water, and dissolves but slowly in sodium carbonate or hydroxide solutions. When the acid is treated with alcoholic phenylhydrazine, it yields no hydrazone, but merely the *phenylhydrazine* salt, $C_{17}H_{15}O_6N_5$, melting at 210°.

Ethyl *p*-nitrobenzeneazoacetonedicarboxylate yields a *phenylhydrazone*, $NO_2\cdot C_6H_4\cdot N_2\cdot CH(CO_2Et)\cdot C(CH_2\cdot CO_2Et){:}N\cdot NHPh$, in the form of red crystals melting at 160°, which readily loses alcohol, yielding two isomeric pyrazolone derivatives. *Ethyl* 1-*phenyl*-4-p-*nitrobenzeneazo*-5-*pyrazolone*-3-*acetate*,  $NO_2\cdot C_6H_4\cdot N_2\cdot CH\left<\begin{array}{l} CO\text{———}NPh \\ C(CH_2\cdot CO_2H) \end{array}\right>N$, forms red crystals melting at 189°, and only sparingly soluble in alcohol; the *acid* forms yellowish-red needles melting and decomposing at 196°, is insoluble in ether, benzene, or chloroform, and when heated slightly above its melting point loses carbon dioxide and yields 1-phenyl-3-methyl-4-*p*-nitrobenzeneazo-5-pyrazolone.

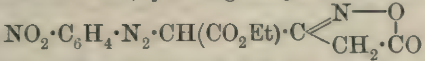
Ethyl 1-*phenyl*-5-*pyrazolone*-3-p-*nitrobenzeneazoacetate*,

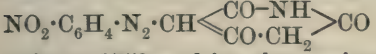


$$NO_2\cdot C_6H_4\cdot N_2\cdot CH(CO_2Et)\cdot C{<}\begin{array}{l}N—NPh\\ CH_2\cdot CO\end{array},$$

crystallises from acetic acid in fine, yellow needles melting and decomposing at 224°, and readily soluble in glacial acetic acid or chloroform; the *acid* crystallises in short, green needles melting and decomposing at 205°.

Ethyl 1-*carbamino*-5-*pyrazolone*-3-p-*nitrobenzeneazoacetate*, obtained by the action of semicarbazide on the original condensation product, crystallises in yellow plates melting at 214—215°, and is readily soluble in acetone or hot acetic acid.

The *oxime* of ethyl *p*-nitrobenzeneazoacetonedicarboxylate crystallises in small, yellow needles melting at 160°, and dissolves in boiling acetic acid, yielding *ethyl* 5-*isooxazolone*-3-p-*nitrobenzeneazoacetate*,  $NO_2\cdot C_6H_4\cdot N_2\cdot CH(CO_2Et)\cdot C{<}\begin{array}{l}N—O\\ CH_2\cdot CO\end{array}$, melting at 162—163°.

Ammonia reacts with ethyl *p*-nitrobenzeneazoacetonedicarboxylate, yielding a compound, $C_{11}H_8O_5N_4$, which crystallises in red needles, melts at 296°, and is probably *β*-p-*nitrobenzeneazo*-*α*-*ketoglutarimide*,  $NO_2\cdot C_6H_4\cdot N_2\cdot CH{<}\begin{array}{l}CO-NH\\ CO\cdot CH_2\end{array}{>}CO$; its *phenylhydrazone*, $C_{17}H_{14}O_4N_6$, melts at 175°, and is only sparingly soluble in the usual solvents.

The original condensation product reacts partly as an azo-compound, and also as a phenylhydrazone, and hence contains a labile hydrogen atom. J. J. S.

Explosiveness of Diazobenzenesulphonic Acid. By HERMANN WICHELHAUS (*Ber.*, 1901, **34**, 11).—A case is described of violent spontaneous explosion of dry diazobenzenesulphonic acid; greater care seems necessary in dealing with it than has been hitherto thought needful. W. A. D.

Precipitation of Proteids by Chloroform. By ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1900, **31**, 329—337. Compare Formánek, Abstr., 1900, i, 532).—Blood serum and many pathological specimens preserved with chloroform assume an opaque appearance, and in some instances a small amount of coagulated albumin is deposited. The albumin of blood serum is not all coagulated when warmed for 24—48 hours at 40° with chloroform, but at 55° the coagulation is complete in a short time. Yolk of egg when mixed with chloroform and water gradually sets to a pulp, and the filtrate from this, even when the mixture has been allowed to remain for years, contains albumin, which is coagulated on heating. Albumose solutions when preserved with chloroform also tend to coagulate, and it appears that heteroalbumose is converted into dysalbumose in contact with chloroform. The filtrate from the dysalbumose contains protalbumoses and deuteroalbumoses, and chloroform is thus capable of separating primary and secondary albumoses.

The casein in milk which has been preserved with chloroform is slowly but completely precipitated. J. J. S.

[Methylmercaptan from Albumin.] By MARCELLUS NENCKI (*Ber.*, 1901, **34**, 201—202).—A claim for priority in the discovery of methylmercaptan as a decomposition product of albumin.

T. M. L.

Acid containing Phosphorus from Casein, and its Iron Compound. By ERNST SALKOWSKI (*Chem. Centr.*, 1901, i, 225; from *Centr.-Bl. med. Wiss.*, **28**, 865—867).—By digesting casein with artificial gastric juice, *paranucleic acid* is formed together with paranuclein. The *iron* salt of this acid, prepared by heating a neutralised solution with a ferric salt, contains 22 per cent. of iron, 2·5 of phosphorus and 9 of nitrogen, and is easily assimilated by animals.

E. W. W.

Globulin as Alkali-proteid. By JOHANNES STARKE (*Zeit. Biol.*, 1900, **40**, 419—446). **Transformation of Albumin into Globulin.** By JOHANNES STARKE (*ibid.*, 494—525).—A number of experiments are adduced to prove that globulin is an alkali-proteid, which, however, is distinguished from the albuminate usually known as alkali-albumin. It is further stated that albumin (from white of egg) can be readily transformed into globulin by diluting with water and heating to 56°.

W. D. H.

Oxidising Action of Ammonium Persulphate on Products of the Animal Organism. By LOUIS HUGOUNENQ (*Compt. rend.*, 1901, **132**, 91—93).—Uric acid is oxidised by ammonium persulphate at the ordinary temperature, and converted into allanturic acid, carbamide, and glycine. In presence of an alkali hydroxide, the reaction is more energetic, but the products are carbamide and ammonium allanturate, the action being similar to that of lead or manganese peroxides, potassium permanganate or ferricyanide, or ozone. Allantoin is probably formed as an intermediate product, but if the proportion of persulphate is reduced with a view to isolate it, the greater part of the uric acid remains unaltered.

Bilirubin in presence of an alkali is completely and instantly converted into biliverdin, and the reaction affords the best method of preparing the latter.

Hæmatin in presence of ammonia is attacked in the cold, and after boiling for two or three minutes, the black solution becomes colourless and a precipitate of ferric hydroxide is formed. This reaction can be utilised for the detection of iron in hæmatin and probably also in hæmoglobin and the ferruginous nucleins.

Blood diluted and mixed with excess of ammonia is oxidised and decolorised after a few hours at the ordinary temperature with production of a pale yellow liquid and a slight ochreous precipitate. The same change is produced in a few minutes on heating. C. H. B.

Methæmoglobin. By RUDOLF KOBERT (*Pfluger's Archiv*, 1900, **82**, 603—630. Compare Abstr., 1886, 637).—The best method for the preparation of methæmoglobin, is to shake a 1—4 per cent. filtered solution of blood (from carnivorous or herbivorous animals) in distilled water with a few small crystals of potassium ferricyanide in the presence of air for a few seconds, and to decant from the undissolved ferricyanide; if oxyhæmoglobin is still present, the operation is repeated. Cow's blood gives some 10 per cent., and dog's blood 15 per cent. of methæmoglobin. In many properties, methæmoglobin resembles acid-hæmoglobin. The characteristic absorption band in the orange when measured in 0·1 per cent. solution in a layer 10 mm. thick gave 630—652 $\mu\mu$.

Alkali methæmoglobin obtained by the action of a few drops of very dilute solution of sodium carbonate, potassium carbonate, lime-water, basic sodium phosphate, ammonia, or an organic base, has two absorption bands near those of acid-hæmoglobin and oxyhæmoglobin, but more feebly developed. It has the same percentage composition as oxyhæmoglobin, but according to the author is a distinct substance, and in the organism is more readily reconverted into oxyhæmoglobin than is ordinary methæmoglobin.

A 1 per cent. solution of methæmoglobin spread out into a layer 3 mm. thick, and exposed to bright sunlight, is completely converted into photomethæmoglobin within 30 minutes; when placed in the dark, it is not reconverted into methæmoglobin. Most of Bock's results are confirmed.

Methæmoglobin forms an unstable compound with hydrogen peroxide, and as the combination takes place readily, the author recommends methæmoglobin as a reagent for hydrogen peroxide, the change in colour being from brown to pale red; the brown colour, however, returns when the mixture is warmed.

Szigeti and Max Richter have stated that the author's cyanomethæmoglobin (Abstr., 1892, 361) is identical with Hoppe-Seyler's cyanohæmatin, but according to the author it is an entirely distinct substance.

Potassium thiocyanate changes the colour and absorption spectrum of methæmoglobin, but whether a definite compound is formed is questionable. Potassium nitrite also causes a change in colour from brown to red.

The existence of a sulphomethæmoglobin is questioned.

Even dilute solutions of hæmoglobin and its derivatives exhibit strong absorption bands in the violet and ultra-violet of the spectrum.

J. J. S.

Decomposition Products of Oxyhæmoglobin from Horses. By D. Lawroff (*Ber.*, 1901, **34**, 101—102. Compare Abstr., 1899, ii, 231).—Some 20·3 per cent. of hexon bases are obtained by the action of hydrochloric acid and tin on oxyhæmoglobin from horses; the bases consist of histidine, arginine, and lysine. J. J. S.

Mechanism of the Action of Enzymes. By Maurice Hanriot (*Compt. rend.*, 1901, **132**, 146—149).—When an enzyme is attenuated by chemical action, it can be regenerated and return to its former activity. The action of lipase on acids and ethers appears to be a chemical combination which obeys the laws of dissociation.

W. D. H.

Action of Nitrous Acid on Wool. By Alexander P. Lidoff (*J. Russ. Phys. Chem. Soc.*, 1900, **32**, 766—774).—The action which hot nitric acid exerts on wool with the production of a yellow colour is found to be due to the nitrous acid formed when the nitric acid is heated, the intensity of the colour increasing with the proportion of nitrous acid present. The colour which nitric acid imparts to wool is, however, perfectly stable towards sunlight, whilst that given by nitrous acid undergoes rapid change, unless the wool be subsequently dipped into cold nitric acid, when the colour becomes stable to light. Experiments made on the change of weight occurring when wool is nitrated showed in the majority of cases a loss of weight varying between 2·19 and 21·9 per cent., although in one case an increase of 1·98 per cent. was observed. The nitrated wool feels coarser to the touch than before treatment, and reacts readily in the cold with ordinary reducing reagents, the yellow colour being converted into a dark brown. The nitrated wool, after perfect washing, is acid towards litmus, and at a temperature of 50—60° decomposes carbonates with the evolution of carbon dioxide, the colour of the wool being changed to brown. It darkens when heated in a vacuum at 110—120° and afterwards chars; it is comparatively readily acted on by dyes. Nitrated wool decomposes potassium iodide solution, with precipitation of iodine, both in the fibre and in the solution. The coefficient of acidity (the number of milligrams of potassium hydroxide fixed by 1 gram of the substance when acted on by seminormal alcoholic potassium hydroxide for 12 hours) of the unaltered wool has a mean value 88, whilst that of the nitrated product is 169. If the nitrated wool after absorption of potassium hydroxide be washed with alcohol until it has a neutral reaction, it will be found to be strongly alkaline on placing in water, owing to the hydrolysis of the unstable alkali compound. Nitrated wool is not hygroscopic, and it contains less nitrogen than the raw material. The iodine values for wool before and after nitration have the mean values 18·4 and 4·7 respectively. The action of nitrous acid on wool may be regarded partly as a saturation of the free bonds of the molecule with nitro- or nitroso-groups, and partly as an action of nitrous acid on the amino-groups present, to which is due the increase produced in the acid functions. T. H. P.

Mercury Organo-metallic Compounds. By AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and CHEVROTIER (*Compt. rend.*, 1901, **132**, 145—146).—*Sodium mercuriphenoldisulphonate*, prepared by treating sodium phenoldisulphonate with mercuric oxide in mol. proportion, is an amorphous, white powder containing about 40 per cent. of mercury; 22 parts of the salt dissolve in 100 parts of water at 15°. A solution of this compound is salt to the taste like that of a sodium salt; it yields no precipitates with sodium hydroxide, hydrochloric acid, ammonium hydrosulphide, or cold albumin solution. The substance possesses the germicidal and antiseptic properties of a mercury salt without its irritating action on the animal membranes. Solutions containing 1/1000th to 1/2000th parts of the compound stop the development of Eberth's bacillus, *B. pyocyaneus*, *B. staphylococcus*, *B. subtilis*, and *B. lactis*, and prevents the putrefaction of blood, meat-infusion or urine. The coefficient of toxicity determined for the rabbit by intravenous injection is 0·039 gram per kilo.; that for the guinea pig by subcutaneous injection is 0·05 gram per kilo. G. T. M.

Organic Chemistry.

Generation of Hydrocarbons by Metallic Carbides. By M. Berthelot (*Compt. rend.*, 1901, **132**, 281—290).—Of the various types of metallic carbides the acetylides are the simplest, being derived from acetylene by the substitution of the hydrogen atoms by two atoms of a univalent, or one atom of a bivalent, metal. Some of these are decomposed by water with the development of heat and the regeneration of acetylene. The condition for the occurrence of this reaction is that $r - q > 196 \cdot 1$, where r is the heat of formation of the acetylide from its elements, and q that of the metallic hydroxide. This condition is fulfilled by the carbides of sodium, lithium, calcium, &c., but not by that of silver. Silver carbide is, however, decomposed by dilute hydrochloric acid, the reaction being rendered possible by the increased development of heat due to the formation of silver chloride. If the alkali acetylide contains an excess of metal, the latter decomposes the water with the formation of hydrogen, which immediately reduces the acetylene to ethane and ethylene, all these reactions taking place with the development of heat. A mixture of acetylene, ethylene, and ethane is thus produced, the relative proportions of these gases being dependent on local conditions. A similar formation of ethylene takes place when cuprous acetylide is decomposed by acids in the presence of zinc. Certain metallic oxides, capable of decomposing water, under certain conditions, with the development of heat, also effect the transformation of acetylene into ethylene. Thus ammoniacal solutions of chromous salts absorb acetylene, and then, almost immediately, evolve ethylene.

Aluminium carbide, Al_4C_3, may be taken as the type of a second class of carbides which are decomposed by water, with the production of methane instead of acetylene. In the case of aluminium carbide, the reaction takes place so slowly that the heat developed cannot be estimated directly, but an approximate value may be calculated from the heat of combustion of the carbide, which was found to be +824 Cal. It is shown from a comparison of thermochemical data that the formation of methane from aluminium carbide corresponds with the greatest possible development of heat. The author lays stress on two principles involved in reactions such as those under consideration, namely, the conservation of the molecular type resulting from the exchange of equal valencies and the tendency towards the production of the maximum thermal effect. Both these principles are satisfied in the decomposition by water of aluminium carbide and, probably, of beryllium carbide, which also furnishes pure methane.

A third class of carbides includes that of manganese, Mn_3C, which furnishes equal volumes of methane and hydrogen, and here also it is shown that the production of acetylene, ethylene, or ethane would result in the development of less heat than that actually observed.

The reactions involved in the decomposition of the carbides of cerium, lanthanum, yttrium, uranium, &c., are more complex, variable mixtures of methane, acetylene, ethylene, and small quantities of liquid hydrocarbons being produced. These results are attributed partly to the fact that the composition of the oxides of the metals referred to does not correspond with that of the carbides; possibly, also, the latter are mixtures or polymerised compounds. N. L.

Composition of Grosny Naphtha. By Michael I. Konowaloff and Mme. A. Plotnikoff (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 50—51).—By the action of concentrated sulphuric acid on a fraction of Grosny naphtha boiling at 160—165°, a considerable proportion of sulphomesitylenic acid was obtained, together with a crystalline compound melting at 210°. The fraction hence contains a large quantity of mesitylene. T. H. P.

Action of Organometallic Derivatives on Alkyl Esters. By Auguste Béhal (*Compt. rend.*, 1901, **132**, 480—482).—When alkylhalogen magnesium compounds act on alkyl esters of the cyclic series, the first stage in the reaction is $R{\cdot}CO_2Et + MgMeI = MgI{\cdot}O{\cdot}CRMe{\cdot}OEt$, and the second stage $MgI{\cdot}O{\cdot}CRMe{\cdot}OEt + MgMeI = MgI{\cdot}OEt + MgI{\cdot}O{\cdot}CRMe_2$. Finally, $MgI{\cdot}O{\cdot}CRMe_2 = MgI{\cdot}OH + CRMe{:}CH_2$, possibly with intermediate formation of the tertiary alcohol. The ethylenic hydrocarbons thus obtained polymerise readily, forming crystalline solids. When oxidised with chromic mixture or permanganate, they yield methyl ketones, and when treated with iodine and mercuric oxide in presence of alcohol, they also yield methyl ketones and not aldehydes, $CIRMe{\cdot}CH_2{\cdot}OH = HI + R{\cdot}CH_2{\cdot}COMe$.

C. H. B.

Mode of Addition of Hypochlorous Acid to the Olefines. By K. Krassusky (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 1—26).—The author has studied the additive products obtained by the combination of hypochlorous acid with the olefine hydrocarbons, *iso*butylene, propylene, and β-methyl-β-butylene. His results confirm the law enunciated in 1876 by Markownikoff, to the effect that when hypochlorous acid combines with an ethylene derivative, the hydroxyl group becomes joined preferably to the carbon atom with which are united the fewest hydrogen atoms. Under unfavourable conditions, the reaction gives rise to secondary products formed by the action of water, acid, and chlorine on the chlorohydrin and the hydrocarbon. The concentration of the hypochlorous acid used has not much influence on the course of the reaction, which, however, depends to some extent on the temperature.

The action of hypochlorous acid on *iso*butylene gives a yield of about 78 per cent. of the theoretical quantity of the chlorohydrin, $OH{\cdot}CMe_2{\cdot}CH_2Cl$, which boils at 126—128° and has the sp. gr. 1·0878 at 0°/0° and 1·0687 at 17·6°/0°. If strong hypochlorous acid is used, the chlorohydrin is accompanied by a considerable proportion of an unsaturated chloro-derivative boiling at 69—70° and having the composition C_4H_7Cl, which is also obtained when *iso*butylene chlorohydrin is heated either with anhydrous oxalic acid or by itself in a sealed tube.

β-Methyl-β-butylene and hypochlorous acid give a 25 per cent. yield of the chlorohydrin, $OH\cdot CMe_2\cdot CHMeCl$, which boils at 141—142°, and has the sp. gr. 1·0546 at 0°/0° and 1·0356 at 18·6°/0°.

By the action of anhydrous oxalic acid or phosphoric oxide, β-methyl-β-butylene chlorohydrin is converted into *β-methyl-γ-chloro-β-butylene*, $CMe_2{:}CMeCl$, which boils at 97—98° and has the sp. gr. 0·9395 at 0°/0° and 0·9215 at 18·1°/0°. The addition of bromine to the latter compound gives rise to a solid *bromo*-derivative, $C_5H_9ClBr_2$, which has the normal molecular weight in freezing benzene.

T. H. P.

Complete Synthesis of Acetylpropylene [Pentinene] and of Terpilenic Hydrocarbons. By MARCELLIN BERTHELOT (*Compt. rend.*, 1901, **132**, 599—606).—When a mixture of equal volumes of acetylene and propylene is heated at about 500° for an hour, a contraction of about one-third takes place, and a nearly colourless, oily liquid, together with a little tarry matter, condenses in the colder parts of the vessel. The greater part of the condensed liquid is readily volatile, and consists of a pentinene, C_5H_8, whilst the smaller, less volatile portion appears to consist of terpilenic hydrocarbons; benzene is not formed in appreciable quantity unless the gases have been too strongly heated. The residual gases, amounting to 63·9 per cent. of the original volume, contained unaltered acetylene and propylene, each 23 vols.; gaseous pentinene, 9 vols.; methane (or an equivalent mixture of saturated hydrocarbons with hydrogen), 8·9 vols.

Similar results are obtained by heating a mixture of acetylene and trimethylene, the latter probably first being transformed into the isomeric propylene. With a mixture of allylene and ethylene, combination also occurs, but more slowly; the liquid product of the reaction consists of hydrocarbons of high boiling point, together with a small quantity of a volatile hydrocarbon, probably allylethylene, isomeric with the preceding pentinene. Allylene and acetylene enter into reaction much more readily, a liquid rich in benzene being obtained, besides an abundance of tarry matter. Propylene and ethylene react very slowly, only a trace of liquid being formed. The final step in the synthesis of terpilenic hydrocarbons is to be sought in the polymerisation and interaction of the two pentinenes already referred to and their isomerides, these being formed, as described above, from hydrocarbons which may themselves be synthetically formed from their elements.

N. L.

αδ-Dibromobutane and αδ-Diiodobutane. New Synthesis of Adipic Acid. By JULES HAMONET (*Compt. rend.*, 1901, **132**, 345—347).—*αδ-Dibromobutane*, $CH_2Br\cdot CH_2\cdot CH_2\cdot CH_2Br$, readily formed by saturating αδ-diamyloxybutane with hydrogen bromide, is a colourless liquid which boils, and partially decomposes, at 196—197°, and has a sp. gr. 1·79 at 18°. *αδ-Diiodobutane*, obtained in a similar manner with almost the theoretical yield, boils with slight decomposition at 125—126° under 15 mm. pressure, and has a sp. gr. 2·307 at 18°. When treated with potassium cyanide, and the resulting nitrile hydrolysed, adipic acid is obtained.

N. L.

Pyrogenic Reactions of Organic Compounds. By WLADIMIR IPATIEFF (*Ber.*, 1901, **34**, 596—600. Compare Marchand, *J. pr. Chem.*, 1838, **15**, 7; Caventon, *Annalen*, 1863, **127**, 93).—When methyl alcohol is passed through a red hot iron tube, considerable quantities of formaldehyde are produced together with combustible gases and about 3 per cent. of carbon. When ethyl alcohol is passed through a glass tube heated at 660—700°, very little decomposition occurs, but when an iron tube heated at 710—750° is employed, considerable amounts of acetaldehyde, paraldehyde and combustible gases are formed together with about 3 per cent. of carbon. *iso*Butyl alcohol under similar conditions gives about 40 per cent. of pure *iso*butaldehyde and *iso*amyl alcohol 30—40 per cent. of the corresponding aldehyde. The author recommends the method as a simple one for the preparation of aldehydes.

Methyl*iso*butylcarbinol gives a 30—40 per cent. yield of methyl *iso*butyl ketone. Tertiary alcohols appear to be more stable, thus when dimethylethylcarbinol is passed through an iron tube heated at 660—700°, the greater part remains unaltered, but at 750—800° an olefine hydrocarbon, water, and combustible gases are produced.

J. J. S.

Action of Alcohol on Metals. By MALMÉJAC (*J. Pharm.*, 1901, [vi], **13**, 169—171).—Iron, tin, zinc, lead, and galvanised iron were allowed to remain in contact with alcohol of 95° for six months at 15°, when it was found that in all cases a small quantity of the metal had gone into solution. Copper, under the same conditions, is entirely unacted on.

H. R. LE S.

Separation of the Amyl Alcohols contained in Fusel Oil. I. By WILLY MARKWALD (*Ber.*, 1901, **34**, 479—484. Compare Pasteur, *Compt. rend.*, 1855, **41**, 296; Le Bel, this Journal, 1874, 139; *Bull. Soc. Chim.*, 1874, [ii], **21**, 542; 1876, [ii], **25**, 545; Rogers, Trans., 1893, **63**, 1130; Balbiano, this Journal, 1877, i, 292).—The reason that the separation of the two amyl alcohols by Pasteur's method is so tedious is that the two barium salts form mixed crystals; the separation of the two salts could probably be more readily accomplished by other methods. Le Bel was in error in assuming that a limit was reached when the quantities of the two amyl alcohols in the mixture were in the inverse ratio of their esterification constants with hydrogen chloride. Using Rogers' data, the ratio of the velocities of esterification of the two amyl alcohols may be calculated, and is found to be $c = 0{\cdot}446$. It is pointed out that if Rogers had completed the process used by him only 30 c.c. of 99 per cent. active amyl alcohol would have been obtained from 16·2 litres of commercial amyl alcohol.

The amount of active alcohol present in the commercial product varies (16·5—27 per cent.), but at the present time the percentage does not appear to be so high as formerly (Ley, *Ber.*, 1873, **6**, 1362).

J. J. S.

Separation of the Amyl Alcohols contained in Fusel Oil. II. By WILLY MARKWALD and ALEXANDER McKENZIE (*Ber.*, 1901, **34**, 485—491 Compare preceding abstract).—The authors have succeeded in separating the two amyl alcohols of fusel oil, *iso*amyl alcohol and β-methylbutyl alcohol, by converting them into acid esters of 3-nitrophthalic acid (compare Wegscheider and Lipschitz, this vol., i, 32). The separation of the two esters is tedious, as they form mixed crystals. 1-iso*Amyl 2-hydrogen 3-nitrophthalate*,

$$NO_2\cdot C_6H_3(CO_2H)\cdot CO_2\cdot C_5H_{11},$$

is obtained when the acid is esterified by the Fischer-Speier method and the product crystallised from carbon disulphide, then from carbon tetrachloride, and finally from benzene until it melts sharply at 95°; it dissolves readily in alcohol, acetone, benzene, or hot carbon tetrachloride, and both it and the alcohol obtained from it are inactive.

To obtain the active amyl alcohol, the commercial product is treated by Rogers' process, except that hydrogen chloride is employed instead of concentrated hydrochloric acid. By this method, an alcohol having a rotation α_D $-5{\cdot}95°$ $(l=2)$ may be obtained; this is then esterified by the Fischer-Speier method, 1 part of 3-nitrophthalic acid being employed for every 2·5 parts of alcohol and 0·23 part of sulphuric acid. The acid ester is mixed with its own volume of carbon disulphide and the residue then crystallised from benzene until it melts sharply at 113·5—114·5°. The crystallisation was so conducted that the mother liquor from a fraction of high melting point was employed for the solution of the fraction with the next highest melting point. *Active* 1-*amyl* 2-*hydrogen* 3-*nitrophthalate* forms well-defined, glistening crystals, fairly readily soluble in most organic solvents, and has $[\alpha]_D$ $+6{\cdot}5°$ at 17°. The active amyl alcohol obtained on hydrolysis boils at 128°, has a sp. gr. 0·816 at 20°/4° and $[\alpha]_D$ $-5{\cdot}90°$ at 20°; its odour is quite different from that of ordinary *iso*amyl alcohol. The numerous derivatives of active amyl alcohol described in detail by Guye, Walden, Frankland, and others are in reality mixtures and were mostly obtained from an alcohol containing some 75—80 per cent. of the active constituent.

J. J. S.

Nitrating Action of Nitric Acid on Derivatives of Saturated Hydrocarbons. II. Action of Nitric Acid on Alcohols. By MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 48—50).—By gradually adding concentrated nitric acid to an acetic acid solution of dimethylethylcarbinol, diluting with water, and neutralising with excess of potassium hydroxide, the liquid separates into two layers. The alcoholic layer contains the nitro-derivative of the alcohol and a crystalline compound melting at 96—97° which is probably the amylene nitrosate, $NO_3\cdot CMe_2\cdot CMe\colon NOH$, described by Wallach. In the aqueous liquor is found the *oxime* of a hydroxy-ketone having the constitution $OH\cdot CMe_2\cdot CMe\colon N\cdot OH$, and melting at 82—84°.

T. H. P.

Syntheses of Tertiary Alcohols of the Fatty Series. By HENRI MASSON (*Compt. rend.*, 1901, **132**, 483—485).—By the action of magnesium methyl iodide and magnesium ethyl iodide on alkyl esters in presence of ether, the author has obtained a number of tertiary alcohols of the fatty series, the group $X\cdot CO_2Et$ being converted into $X\cdot CRR'\cdot OH$. He has thus prepared dimethylpropylcarbinol (b. p. 124°), diethylpropylcarbinol (b. p. 159°), *diethyl*iso-

butylcarbinol boiling at 172°, *dimethylamylcarbinol* boiling at 162°, *diethylamylcarbinol* boiling at 199°, *dimethylhexylcarbinol* boiling at 178°, and *diethyloctylcarbinol* boiling at 250°. They are all liquids lighter than water, boil without decomposing under normal pressure, and are volatile in steam. When mixed with a little ethyl alcohol, but not otherwise, they yield a precipitate with Denigès' reagent. With iodine and phosphorus, they yield iodo-derivatives, which do not boil without decomposing but are volatile in steam. When these iodo-derivatives are treated with alcoholic potash, they yield olefines, but the best method of obtaining these hydrocarbons is to heat the tertiary alcohols with acetic anhydride; under these conditions, diethylpropylcarbinol yields *γ-ethyl-β-hexene*, $CH_2Me\cdot CH_2\cdot CEt\dot{:}CHMe$, boiling at 119—120°. C. H. B.

Action of Esters of Monobasic Fatty Acids on Mixed Organomagnesium Compounds. By VICTOR GRIGNARD (*Compt. rend.*, 1901, **132**, 336—338. Compare Abstr., 1900, i, 382).—The first product of the action of magnesium ethyl bromide on ethyl formate appears to be an additive compound, $OEt\cdot CHEt\cdot OMgBr$, which is converted by the further action of the magnesium ethyl bromide into the compound $CHEt_2\cdot OMgBr$; the latter is decomposed by water with the formation of diethylcarbinol. The action of magnesium *iso*amyl bromide on ethyl formate results in the formation, not, as was expected, of di*iso*amylcarbinol, but of the corresponding *formate*, a colourless liquid of faint, agreeable odour, which boils at 100—101° under 8 mm. pressure. The molecular refraction (59·94—60·171) of this compound accords better with the constitution

$$C_5H_{11}\cdot C(OH)\dot{:}C(OH)\cdot C_5H_{11}$$

than with the normal formula. *Diisoamylcarbinol*, obtained by the hydrolysis of the preceding compound, is a colourless liquid which boils at 105° under 9 mm. pressure. The action of magnesium *iso*butyl bromide on ethyl formate yields a mixture of *diisobutylcarbinol*, which boils at 172—174° under 752 mm. pressure, and the corresponding *formate*, which boils at 173—175° under 750 mm. pressure.

Magnesium methyl iodide reacts with methyl acetate to form trimethylcarbinol, whilst magnesium *iso*amyl bromide yields *methyldiiso-amylcarbinol*, which boils at 108—109° under 10 mm. pressure.

N. L.

Methylbutylallylcarbinols containing Normal and Secondary Butyl. By KONSTANTIN TALIEFF (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 26—35).—*Methylbutylallylcarbinol*, $C_9H_{18}O$, prepared by the action of zinc on methyl butyl ketone (1 mol.) and allyl iodide (1·5 mols.), is a colourless liquid which boils at 179·1°, is insoluble in water, and has a characteristic odour somewhat resembling that of turpentine. It has the sp. gr. 0·84412 at 20°/0° and 0·84497 at 20°/20°, and n_α 1·43990, n_β 1·44857, and n_γ 1·45361. Its *acetyl* derivative, $C_{11}H_{20}O_2$, is a colourless liquid boiling at 196—201° and possessing a pleasant ethereal odour slightly recalling that of turpentine.

Methylsec.butylallylcarbinol, obtained by the action of zinc on methyl *sec.*butyl ketone and allyl iodide, is a colourless liquid boiling at 174·9° and having a faint turpentine-like odour. It is insoluble in water and has the sp. gr. 0·85438 at 20°/0° and 0·85526 at 20°/20°, n_α 1·44460, n_β 1·45324, and n_γ 1·45850. Its *acetyl* derivative boils at about 190—195°.

When gently oxidised with potassium permanganate solution, both these alcohols yield the corresponding *trihydric alcohols* of the constitution $OH\cdot CMePr\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$, which are obtained as thick syrups readily soluble in water or alcohol, and to a less extent in ether. When more energetically oxidised, the trisubstituted carbinols yield the corresponding *methylbutylhydracrylic acids*, $C_8H_{16}O_3$, in the form of thick syrups; the *calcium*, *barium*, *zinc* and *silver* salts of both acids were prepared. T. H. P.

New Diprimary Glycol. αδ-Butanediol or Tetramethylene Glycol and its Diacetin. By Jules Hamonet (*Compt. rend.*, 1901, **132**, 631—633).—The *diacetin*, $OAc\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OAc$, obtained by treating αδ-diiodobutane with a mixture of silver acetate and acetic acid, crystallises in large, arborescent needles melting at 12° and boiling at 124° and 230°, under pressures of 20 and 751 mm. respectively; it has a sp. gr. 1·048 at 20°. *αδ-Butanediol*, $OH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$, obtained by the hydrolysis of the preceding compound, is a viscous, colourless liquid, miscible in all proportions with water, has a sp. gr. 1·020 at 20° and boils at 230° under 759 mm. pressure; when cooled to 0°, it is slowly converted into crystals melting at 16°. It does not dissolve cupric hydroxide in presence of alkalis, and is easily separated from water by addition of potassium carbonate. N. L.

Pentahydric Alcohol from Propyldiallylcarbinol. By Dmitri Marko (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 36—38).—By the action of potassium permanganate on propyldiallylcarbinol, an *alcohol* of the constitution $CH_2Me\cdot CH_2\cdot C(OH)[CH_2\cdot CH(OH)\cdot CH_2\cdot OH]_2$ is obtained. Its *penta-acetyl* derivative was prepared. T. H. P.

Action of Zinc Powder on Saturated Fatty Acids. By Alexandre Hébert (*Compt. rend.*, 1901, **132**, 633—635).—When commercial stearic acid is distilled with dry zinc powder at 350—400°, carbon dioxide, hydrogen, and gaseous hydrocarbons, chiefly unsaturated, are evolved, whilst the distillate consists of a little water and about 70 per cent. of a mixture of liquid and solid hydrocarbons of the ethylene series, ranging from $C_{17}H_{34}$ to $C_{90}H_{180}$. This mixture has been submitted to fractional distillation, and the various fractions analysed, and their bromine additive products examined. N. L.

Preparation of Methyl Acrylate. By Otto Röhm (*Ber.*, 1901, **34**, 573—574).—An 80 per cent. yield of dibromopropyl alcohol may be obtained by the addition of bromine to allyl alcohol; this is then oxidised by Biilmann's method (*J. pr. Chem.*, 1900, [ii], **61**, 216), esterified by Caspary and Tollens' process (*Annalen*, 1872, **167**, 247), and treated with zinc. A 77 per cent. yield of methyl acrylate is obtained when the dibromo-ester (550 grams) is gradually run into a mixture of zinc foil (200 grams) and methyl alcohol (200 grams) contained in a reflux apparatus. J. J. S.

Conversion of Dimethylacrylic Acid into Dimethylpyruvic Acid. By Louis Bouveault and A. Wahl (*Compt. rend.*, 1901, **132**, 416—418. Compare this vol., i, 4 and 114).—*Ethyl dimethylpyruvate*, $CHMe_2 \cdot CO \cdot CO_2Et$, produced by heating at 100° the hydrochloric acid solution of ethyl α-aminodimethylacrylate, is a liquid boiling at 65—69° under 15 mm. pressure, and of sp. gr. 1·031 at 0°/0°. The *oxime* forms colourless needles melting at 55°; it is very soluble in all neutral solvents except water and light petroleum. The *semicarbazone* separates from a mixture of ether and light petroleum in the form of colourless prisms and melts at 95—96°.

Dimethylpyruvic acid, obtained by heating its ethyl salt with water at 140—150°, melts at 31°, and boils at 65—67° under 10 mm. pressure; it is very soluble in water, alcohol, or ether. The *oxime* crystallises from ether in white leaflets and melts at 163—165°; the *phenylhydrazone* crystallises from alcohol in yellow needles and melts at 156—157°.

G. T. M.

Distillation of Castor Oil. By Hermann Thoms and Georg Fendler (*Arch. Pharm.*, 1901, **239**, 1—6).—When castor oil is distilled, undecenoic acid and heptaldehyde are obtained, the thermometer rising to about 280°. When about half of the oil has passed over, the residue suddenly swells up, forming a substance like indiarubber in consistency. This was washed with alcohol, chloroform, and ether in succession, and was then found to have the composition $C_{33}H_{58}O_5$, corresponding to the *anhydride* of *triundecenoic acid*. It was hydrolysed with alcoholic potash; the product was found to yield a *hexadecenoic acid*, $C_{16}H_{30}O_2$, melting at 36°, when fused with potassium hydroxide; sebacic acid and an *acid*, $C_{13}H_{22}O_4$, when oxidised with fuming nitric acid; and sebacic and lower fatty acids when oxidised with permanganate. If the distillation of the castor oil is stopped just before the swelling up would otherwise take place, the oily residue yields glycerol, when hydrolysed with alcoholic potash, and the same product as was obtained by hydrolysing the solid residue. This oily residue has the composition $C_{105}H_{184}O_{18}$, corresponding to the *glyceride* of triundecenoic acid; when it swells up on heating, the presumption is that it decomposes into water, acraldehyde, and triundecenoic anhydride.

C. F. B.

New Reactions of Organometallic Derivatives. Alkyl Esters of α-Alkyl-β-ketonic Acids. By Edmond E. Blaise (*Compt. rend.*, 1901, **132**, 478—480).—The alkyl esters of the α-alkyl-β-ketonic acids are obtained by condensing nitriles with the alkyl esters of the α-bromoacetic acids in presence of zinc. The reaction takes place readily with the α-cyclic nitriles, benzonitriles, and cyclic *p*-nitriles, but not with cyclic *o*-nitriles. Cyclic nitriles in which the nitrogen is attached to a side chain, as in benzyl cyanide, readily undergo the condensation. The method is general, and the yield varies from 25 to 50 per cent. The salts are readily converted into ketones by treatment with boiling aqueous solutions of alkali hydroxides.

Ethyl propionylisopropylacetate, $CH_2Me \cdot CO \cdot CHPr^{\beta} \cdot CO_2Et$, from ethyl bromo*iso*valerate and propionitrile, boils at 108—109° under 21 mm. pressure. *Ethyl butyrylisobutyrate*, $CH_2Me \cdot CH_2 \cdot CO \cdot CMe_2 \cdot CO_2Et$, from ethyl bromo*iso*butyrate and butyronitrile, boils at 108—110° under

29 mm. pressure. The corresponding *propyl* iso*propyl ketone* boils at 129—130°, and its *semicarbazone* melts at 117—118°. *Ethyl* iso*hexoyl*-iso*butyrate*, $CHMe_2·CH_2·CH_2·CO·CMe_2·CO_2Et$, from ethyl bromo*iso*butyrate and *iso*hexonitrile, boils at 121—124° under 20—22 mm. pressure and yields iso*propyl* iso*amyl ketone* which boils at 171—172°, whilst its *semicarbazone* melts at 98—99°. *Ethyl* p-*toluoyl*iso*butyrate*, $C_6H_4Me·CO·CMe_2·CO_2Et$, from *p*-toluonitrile and ethyl bromo*iso*butyrate, boils at 169—172° under 25 mm. pressure. *Ethyl phenacetyl*iso*butyrate*, $CH_2Ph·CO·CMe_2·CO_2Et$, from benzyl cyanide and ethyl *iso*butyrate, boils at 164—165° under 16 mm. pressure, and solidifies when cooled. The corresponding *benzyl* iso*propyl ketone* boils at 234—235°, and its *semicarbazone* melts at 140—141°. C. H. B.

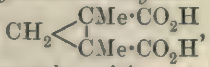
Resolution of Trimethylsuccinic Acid into its Optical Antipodes. By VINCENZO PAOLINI (*Gazzetta*, 1900, **30**, ii, 506—510).—On adding boiling aqueous trimethylsuccinic acid to an alcoholic solution of quinine and cooling the liquid, the salt of the dextro-modification of the acid separates out in radiating, white, silky needles, whilst quinine *l*-trimethylsuccinate can be recovered from the mother liquors.

Quinine d-*trimethylsuccinate*, $C_{20}H_{24}O_2N_2,C_7H_{12}O_4$, melts at 198°. d-*Trimethylsuccinic acid*, when crystallised from water, melts at 140° and has $[\alpha]_D + 4·83°$. With acetyl chloride and a benzene solution of aniline, it yields lævorotatory *anil*-d-*trimethylsuccinic acid*, $C_{13}H_{15}O_2N$, which separates from dilute alcohol in white, feathery needles melting at 130—135° and insoluble in sodium hydroxide solution.

Quinine l-*trimethylsuccinate* crystallises from dilute alcohol in white, radiating, silky needles melting at 188°. l-*Trimethylsuccinic acid* melts at 140° and has $[\alpha]_D - 1·31°$. *Anil*-l-*trimethylsuccinic acid* melts at about 140° and is dextrorotatory. T. H. P.

Polymerisation of Unsaturated Acids. III. α-Methyleneglutaric Acid, a Product of the Polymerisation of Acrylic Acid. By HANS VON PECHMANN and OTTO RÖHM (*Ber.*, 1901, **34**, 427—429).—When methyl acrylate, dissolved in anhydrous ether, is treated with sodium methoxide, it is polymerised to an oil which, when hydrolysed with dilute hydrochloric acid, yields *α-methyleneglutaric acid*, $CO_2H·C(CH_2)·CH_2·CH_2·CO_2H$, as a voluminous crystalline powder; this softens at 125—126°, melts at 129—130°, and forms a *hydrobromide* which melts at 112° and, when reduced with sodium amalgam, yields α-methylglutaric acid. R. H. P.

A New Trimethylenedicarboxylic Acid. By VINCENZO PAOLINI (*Gazzetta*, 1900, **30**, ii, 497—505).—By the action of phosphorus pentachloride on ethyl trimethylhydroxysuccinate, Komppa (Abstr., 1896, i, 597) obtained ethyl chlorotrimethylsuccinate. By carrying out the reaction in chloroform solution and heating the mixture on the water-bath until the evolution of hydrogen chloride ceases, the author obtained a liquid boiling at 110—115° under 15 mm. pressure, which proves to be *ethyl dimethyltrimethylenedicarboxylate*.

Dimethyltrimethylenedicarboxylic acid,  $CH_2<\begin{matrix}CMe·CO_2H\\|\\CMe·CO_2H\end{matrix}$, separates from water in aggregates of prismatic crystals melting at 153—154°.

It is stable towards permanganate and does not take up bromine. The *calcium* salt, with $1H_2O$, was analysed.

Acetyl chloride converts the acid into its anhydride, which was not separated but was directly converted into the *anilide* of the acid, $CO_2H\cdot C_3H_2Me_2\cdot CO\cdot NHPh$, separating from alcohol in feathery, white needles melting at 157°. When heated at about 170°, the latter gives up water and yields the corresponding *anil* acid, $C_{15}H_{13}O_2N$, which separates from dilute alcohol in white, silky needles melting at 105°.

T. H. P.

Formaldehyde. By Carl D. Harries (*Ber.*, 1901, **34**, 635—637).—Solid formaldehyde can readily be obtained by distilling pure paraformaldehyde and condensing the vapour in liquid air. The melting point, determined with a toluene thermometer, was found to be about −92°.

T. M. L.

Formation and Decomposition of Acetals. By Marcel Delépine (*Compt. rend.*, 1901, **132**, 331—334. Compare this vol., i, 3, and ii, 6).—The formation of acetals is a limited reaction and the laws regulating the production and decomposition of these compounds are similar to those observed in the analogous cases of esterification and hydrolysis. In this connection, the behaviour of methylal, the formals of ethyl and propyl alcohols, the formals of glycol, erythritol, and mannitol, and the acetal of mannitol has been studied. In each case, the same final limit is reached whether the starting point is the system, alcohol–aldehyde or formal–water. The limiting proportion of formal or acetal produced is decreased by the presence of water, but increased by the use of an excess of either alcohol or aldehyde (more especially of the former), by rise in temperature, and by addition of acids. Acids are peculiarly efficacious in facilitating the reaction, and are, perhaps, necessary for decomposition. The nature of the acid and its concentration, if the latter is not too great, are without influence on the result. The decomposition and formation of systems reacting in presence of hydrochloric acid may be represented as a function of the time by the usual logarithmic curves.

N. L.

Condensation of *iso*Valeraldehyde with Acetaldehyde. By Alfred Wogrinz (*Monatsh.*, 1901, **22**, 1—13).—This condensation is best effected by the use of a saturated solution of potassium carbonate. The *aldol*, $C_7H_{14}O_2$, which is formed is a colourless liquid and distils at 100—110° under 25 mm. pressure; when freshly distilled, it is unimolecular, but when kept, polymerises into a viscous bimolecular modification. The *oxime* boils at 144° under 25 mm. pressure. Oxidation produces, together with other acids, a viscid, liquid *hydroxy-acid*, $C_7H_{14}O_3$. By long heating, the aldol passes into an *unsaturated aldehyde*, $C_7H_{12}O$, which boils at 149—150° under atmospheric pressure, and on oxidation yields *iso*valeric, acetic, oxalic, and an unknown acid.

K. J. P. O.

Condensation of *iso*Butaldehyde with Crotonaldehyde. By Richard Plattensteiner (*Monatsh.*, 1901, **22**, 14—20).—By condensation of *iso*butaldehyde with crotonaldehyde by aid of a 20 per cent. solution of potassium carbonate, an *aldol*, $C_8H_{14}O_2$, was obtained as a yellow oil which decomposed at 80° and could not be distilled. The *oxime*, $C_8H_{15}O_2N$, is an oil. Reduction with aluminium amalgam converts the aldol into a *dihydric alcohol*, $C_8H_{16}O_2$, a dark yellow oil boiling at 127—134° under 18 mm. pressure; the *diacetate*, $C_8H_{14}O_2Ac_2$, boils at 127—132° under 15 mm. pressure, and forms a dibromo-additive product. The dihydric alcohol is also obtained by the action of alcoholic potassium hydroxide on a mixture of *iso*butaldehyde and crotonaldehyde. K. J. P. O.

Condensation of *iso*Butaldehyde with Propaldehyde. By Moriz Kohn (*Monatsh.*, 1901, **22**, 21—58).—By the action of a saturated solution of potassium carbonate, the aldehydes are condensed to the *aldol*, $CHMe_2·CH(OH)·CHMe·CHO$, a colourless, oily liquid, boiling at 98—100° under 20 mm. pressure. The *oxime*, $C_7H_{15}O_2N$, a colourless thick oil, boils at 144° under 21 mm. pressure. On oxidation, propionic acid and β-hydroxy-αγ-dimethylvaleric acid are obtained, the latter of which melts at 97°. Reduction with aluminium amalgam produces a *heptylene glycol*, $CHMe_2·CH(OH)·CHMe·CH_2·OH$, which crystallises in aggregates of needles, melts at 58—59°, and boils at 117—118° and 215—216° under pressures of 17 and 740 mm. respectively; the *diacetate*, $C_7H_{14}O_2Ac_2$, boils at 116—117° and 226—227° under pressures of 18 and 748 mm. respectively.

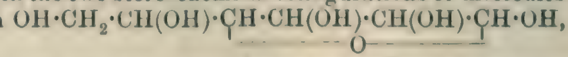
On heating the aldol with a saturated solution of sodium acetate, a *hepteno-aldehyde*, $CHMe_2·CH\!:\!CMe·CHO$, is formed; it is best prepared by the action of dilute aqueous sodium hydroxide on a mixture of *iso*butaldehyde and propaldehyde. It boils at 146—148°, oxidises in the air, and absorbs bromine. The *oxime*, $C_7H_{13}ON$, boils at 100° under 17 mm. pressure, and when heated with acetic anhydride is converted into an *acetate*, $C_7H_{12}ONAc$, boiling at 122° under 17 mm. pressure. When heated at 180° with acetic anhydride, the oxime yields a *heptenonitrile*, $C_7H_{11}N$, a colourless, mobile oil, which boils at 62—64° under 18 mm., and 162—164° under atmospheric pressure. On hydrolysis of the latter by sulphuric acid or potassium hydroxide, αγ-dimethyl-α-butenoic acid (Abstr., 1899, i, 331) is formed. This same acid is formed by atmospheric oxidation of the unsaturated aldehyde, and on more vigorous oxidation is converted into *iso*butyric and acetic acids. K. J. P. O.

Acetaldol [Aldol]. By Jakob H. Halpern (*Monatsh.*, 1901, **22**, 59—65).—The condensation of acetaldehyde to aldol can be effected by means of dry potassium or sodium carbonate, and of aqueous solutions of sodium carbonate or sodium acetate, but not by calcium hydroxide, alcoholic potassium hydroxide, or lead monoxide. The method preferred is that of Orndorff and Newbury (Abstr., 1892, 1423), in which aqueous potassium carbonate is used. Aluminium amalgam reduces aldol or paraldol to butylene glycol. Freshly distilled aldol is unimolecular, whilst its polymerides, the viscid variety and paraldol, are bimolecular. K. J. P. O.

Action of Hydrazine Hydrate on α-Methyl-β-ethylacraldehyde. By Fritz Demmer (*Monatsh.*, 1901, **22**, 69—76).—When α-methyl-β-ethylacraldehyde is warmed on the water-bath with hydrazine hydrate, an *aldazine*, $C_{12}H_{20}N_2$, is formed, which crystallises in pale yellow needles, melts at 54—55°, and boils at 150° under 20 mm. pressure. It unites with 4 atoms of bromine, and is hydrolysed by hydrochloric acid into its constituents. On reduction, ammonia is produced. K. J. P. O.

Action of Potassium Hydroxide on β-Hydroxy-αα-dimethylpropaldehyde (An Analogue of Cannizzaro's Reaction in the Aliphatic Series). By LEO WESSELY (*Monatsh.*, 1901, **22**, 66—68. Compare Abstr., 1900, i, 428).—The formula of this hydroxyaldehyde shows analogies with that of benzaldehyde, as the $\cdot CHO$ group is combined with a carbon atom to which no hydrogen is attached. In addition, similarity is exhibited in certain physical constants, and in the reaction with potassium hydroxide, which is expressed by the equation, $2OH\cdot CH_2\cdot CMe_2\cdot CHO + KOH = OH\cdot CH_2\cdot CMe_2\cdot CH_2\cdot OH + OH\cdot CH_2\cdot CMe_2\cdot CO_2K$. The yields of pentaglycol (αγ-dihydroxy-ββ-dimethylpropane) and the hydroxy-acid (hydroxypivalic acid) are nearly quantitative. K. J. P. O.

Synthesis of Methylheptenone. By WLADIMIR IPATIEFF (*Ber.*, 1901, **34**, 594—596. Compare Tiemann and Semmler, Abstr., 1895, i, 646; Barbier and Bouveault, 1896, i, 55, 637; Verley, 1898, i, 557).—A fairly good yield of *ethyl δδ-dimethylallylacetoacetate*, $CMe_2{:}CH\cdot CH_2\cdot CHAc\cdot CO_2Et$, may be obtained by the condensation of ethyl sodioacetoacetate and αγ-dibromo-γ-methylbutane. It is a colourless liquid, distilling at 120—122° under 11—12 mm. pressure, and when boiled with baryta water or dilute alcoholic potash yields methylheptenone identical in all properties with the product obtained from natural sources. J. J. S.

Constitution of Dextrose. By L. J. SIMON (*Compt. rend.*, 1901, **132**, 487—490).—The author considers that the isomerism of the pentacetates, phenylhydrazones, chloraloses, and glucosides derived from dextroses, and the α- and γ-modifications of the dextroses themselves, is not of the same order as the isomerism between the different hexoses, since all the former are readily reconverted into the parent substance without yielding any other hexose. In all cases, the rotatory power of the β-dextroses is intermediate between, and approximates to the mean of, the rotatory powers of the α- and γ-modifications, and this is true also of the methylglucosides of Fischer. The author explains these facts by assuming that dextrose is tautomeric, the β-modification having the constitution represented by the ordinary aldehydic formula, whilst the α- and γ-modifications, which show mutarotation, correspond with the two stereochemical configurations of molecules of the constitution  $OH\cdot CH_2\cdot CH(OH)\cdot \underbrace{CH\cdot CH(OH)\cdot CH(OH)\cdot CH}_{O}\cdot OH$, containing an additional asymmetric carbon atom. From this point of view, the hydrazones, oximes, &c., correspond with the α- and γ-modifications, but since modifications may also exist with the aldehydic constitution, these compounds may be expected to show mutarotation. C. H. B.

The Phenylhydrazones of Dextrose and their Mutarotation. By L. J. SIMON and H. BÉNARD (*Compt. rend.*, 1901, **132**, 564—566).—The mutarotation of Skraup's phenylhydrazone of *d*-dextrose may be expressed by the exponential equation, $[\alpha]_D^{20°} = -52·9° + 53·67_e^{-0·0044133t}$, where t is time expressed in minutes. This expression indicates that, initially, the substance should be slightly dextrorotatory; the first reading in aqueous solution gave $[\alpha]_D$ as $-6·84°$, after 24 hours the optical activity reached its maximum, and the final observation gave a rotation of $-52·9°$. When the substance is dissolved in alcohol, the optical activity remains constant for several hours, $[\alpha]_D$ being $-8°$; after 6 hours, the rotation increases and the limiting value $-22·5°$ is reached after 36 hours. The presence of potassium hydroxide or dilute hydrochloric acid accelerates the change of rotation without affecting the final value, the acceleration being greater in the case of the acid; the hydrazone becomes, however, partially hydrolysed in moderately concentrated acid solution. Fischer obtained a *d*-dextrose phenylhydrazone melting at 115—116°, whereas Skraup's compound melts at 144° (Abstr., 1887, 567). The authors were not able to obtain Fischer's hydrazone in a state of purity, their preparations always containing a certain amount of the isomeride.

A 4 per cent. solution of a specimen melting at 125° gave, after 25 minutes, a rotation $-66·57°$; the optical activity then decreased regularly until, after 36 hours, its limiting value was reached and found to be identical with that of Skraup's isomeride. The results are in accordance with those observed by Tanret in studying the rotation of the α- and γ-modifications of dextrose (compare Abstr., 1895, i, 490).

G. T. M.

Isomeric Acetyl Halogen Derivatives of Dextrose. By EMIL FISCHER and E. FRANKLAND ARMSTRONG (*Sitzungsber. Akad. Wiss. Berlin*, 1901, **13**, 316—322. Compare Abstr., 1894, i, 3).—The isomeric pentacetyldextroses, when treated with dry hydrogen chloride or bromide in the liquid form, yield the corresponding acetylchloro- or acetylbromo-dextroses. *β-Tetracetylchlorodextrose*, obtained from the pentacetyldextrose melting at 134°, crystallises from light petroleum in aggregates of colourless needles and melts at 73—74°; the yield is almost quantitative. The compound is converted into tetracetyl-β-methylglucoside by the action of finely divided silver carbonate suspended in methyl alcohol; the reaction, however, takes place more slowly than in the case of the corresponding bromo-derivative. The chloro-derivative may be prepared without the use of liquid hydrogen chloride by saturating with the gas a solution of pentacetyldextrose in acetic anhydride at $-20°$, and then heating the mixture in sealed tubes at 45°. β-Tetracetylbromodextrose, obtained by the use of liquid hydrogen bromide, is identical with the compound prepared by Königs and Knorr (Abstr., 1889, 952).

α-Tetracetylchlorodextrose obtained from the pentacetyldextrose melting at 112°, crystallises from light petroleum in colourless needles and melts at 63°.

Tetracetyl-α-methylglucoside, produced by treating the preceding compound with silver carbonate, crystallises from water in lustrous prisms and melts at 100—101°; this substance yields α-methylglucoside on boiling with baryta water.

α-Tetracetylbromodextrose crystallises in colourless prisms and melts at 79—80°. It is less stable than its chlorine analogue and slowly decomposes on keeping.

Tetracetylchlorogalactose, prepared from the pentacetylgalactose melting at 142°, crystallises in spherical aggregates of prisms, and melts at 74—75° (compare Abstr., 1889, 1131). G. T. M.

Carbamide Derivatives of Sugars. By N. Schoorl (*Proc. K. Akad. Wetensch., Amsterdam*, 1901, **3**, 459—462).—*Dextrose-ureide*, $C_6H_{12}O_5\dot{:}N\cdot CO\cdot NH_2$, obtained by heating dextrose (1 mol.) and carbamide (2 mols.) with 5 per cent. sulphuric acid at 50° for 20 days, melts at 206°, has $[\alpha]_D$ $-23°$ at 15° (in 1 per cent. aqueous solution) and is hydrolysed by dilute acids.

Dextrosephenylureide, obtained in a similar manner from dextrose and phenylcarbamide, melts at 223° and has $[\alpha]_D$ $-55°$ (in 1 per cent. solution). Lactose, galactose, mannose, arabinose, and xylose also condense with carbamide. Since methyl-, phenyl-, benzyl-, thio- and phenylthio-carbamides all condense with dextrose, whilst *sym*-disubstituted carbamides do not, it appears that these ureides have a constitution similar to that of oximes and phenylhydrazones. R. H. P.

Synthetic Action of Yeast Maltase. By Oskar Emmerling (*Ber.*, 1901, **34**, 600—605).—On repeating Hill's experiments (Trans., 1898, **73**, 634) as to the action of yeast maltase on pure dextrose, the author finds that not maltose but *iso*maltose is the disaccharide formed; the action of the enzyme on maltose is therefore not truly reversible as considered by Hill, but is similar in character to that of the mineral acids, which are capable of converting dextrose into *iso*maltose (Fischer, Abstr., 1891, 412; 1896, i, 119). The osazone isolated by Hill melting at 178—180° was probably a mixture of glucosazone and *iso*maltosazone, not maltosazone which melts at 206°. In the author's experiments, the *iso*maltose was isolated in the form of its osazone (m. p. 149—152°) after destroying the excess of dextrose by fermentation with a pure yeast incapable of affecting maltose. The yield was in all cases small. W. A. D.

Constitution of Gentianose. By Émile Bourquelot and Henri Hérissey (*Compt. rend.*, 1901, **132**, 571—574. Compare Abstr., 1898, i, 597).—Gentianose, $C_{18}H_{32}O_{16}$, a sugar extracted from the fresh gentian root, is a hexotriose hydrolysed by the action of invertase or very dilute sulphuric acid (0·2 per cent.) into a new hexobiose *gentiobiose*, $C_{12}H_{22}O_{11}$, and lævulose; more concentrated acid or the fermenting extract of *Aspergillus niger* hydrolyses it completely into 1 mol. of lævulose and 2 of dextrose. Gentiobiose has not yet been obtained crystalline, but it is nevertheless a definite compound resembling maltose; its osazone is soluble in hot water, crystallises on cooling the solution, and melts at 142°; it is feebly dextrorotatory $[\alpha]_D$ being 7·7°. In cupric-reducing power, 0·083 gram of the new sugar is equivalent to 0·05 gram of invert sugar. When treated in the cold with an extract of *Aspergillus*, or when heated to 110° with 3 per cent. sulphuric acid, gentiobiose is hydrolysed into 2 mols. of dextrose.

G. T. M.

Regularities in the Melting Points of Aliphatic Diamines. By FELIX KAUFLER (*Chem. Zeit.*, 1901, **25**, 133).—It is pointed out that in the homologous series of aliphatic diamines with the amino-groups at the ends of the chain, the compounds with an odd number of carbon atoms have relatively lower melting points than those with an even number of carbon atoms, thus:—Ethylenediamine, + 8·5°, trimethylenediamine, liquid; tetramethylenediamine, 27°; pentamethylenediamine, liquid; hexamethylenediamine, 40°; octomethylenediamine, 51°; nonomethylenediamine, 37°; decamethylenediamine, 61°.

J. J. S.

isoPropanolamine [β-Aminoisopropyl Alcohol]. By EDGAR PEETERS (*Bull. Acad. Roy. Belg.*, 1901, 9—16).—The author has reduced β-nitroisopropyl alcohol (Abstr., 1895, i, 638), best with tin and hydrochloric acid, to *β-amino*iso*propyl alcohol*, $NH_2\cdot CH_2\cdot CHMe\cdot OH$. This substance boils at 160—171° under 750 mm. pressure, has a sp. gr. 0·973 and n_D 1·45 at 18°; its molecular weight, determined cryoscopically in acetic acid solution, is normal; its vapour density, however, as determined by Hofmann's method under pressures of 120—180 mm., decreases from 0·7 to 0·5 of the normal as the temperature rises from 100 to 185°, whilst as determined by V. Meyer's method at 185°, it is 1·45 times the normal value. The base forms a *platinichloride* and a *picrate* melting at 195° and 142° respectively; also a *dibenzoate* melting at 87°.

C. F. B.

Alcohol Bases. By HERMANN MATTHES (*Annalen*, 1901, **315**, 104—137). Compare Abstr., 1898, i, 399).—The *picrolonates* of methylhydroxyethylamine and ethylhydroxyethylamine melt and decompose at 239° and 245° respectively.

Hydroxyethylpropylamine, $OH\cdot CH_2\cdot CH_2\cdot NHPr^a$, prepared from propylamine and ethylene oxide, is a colourless oil which quickly absorbs water and carbon dioxide; it boils at 182° under 746 mm. pressure, has a sp. gr. 0·9005 at 20°/4°, and n_D 1·4428 at 20°. The *hydrochloride* is hygroscopic, the *platinichloride* is an oil, and the *aurichloride* melts at 85°, whilst the *picrate* and *picrolonate* melt at 104—106° and 238° respectively.

Hydroxyethylbutylamine, $OH\cdot CH_2\cdot CH_2\cdot NH\cdot C_4H_9$. boils at 199—200° under 756 mm. pressure, has a sp. gr. 0·8907 at 20°/4°, and n_D 1·4437 at 20°. The *hydrochloride* is excessively hygroscopic, whilst the *picrate* and *picrolonate* melt at 98° and 218° respectively.

Hydroxyethylhexylamine, $OH\cdot CH_2\cdot CH_2\cdot NH\cdot C_6H_{13}$, boils at 231° under 747 mm. pressure, has a sp. gr. 0·8829 at 20°/4°, and n_D 1·4472 at 20°. The *hydrochloride*, *aurichloride*, and *platinichloride* are deliquescent, whilst the *picrate* crystallises in pale yellow prisms melting at about 80°; the *picrolonate* melts and decomposes at 208—210°.

Hydroxyethylheptylamine, $OH\cdot CH_2\cdot CH_2\cdot NH\cdot C_7H_{15}$, melts at about 35°, and boils at 250—253° under 751 mm. pressure; it has a sp. gr. 0·8819 at 20°/4°, and n_D 1·4510 at 20°. The *hydrochloride*, *aurichloride*, and *platinichloride* are hygroscopic, whilst the *picrate* and *picrolonate* melt at 70—71° and 196° respectively.

*Hydroxyethyl*iso*propylamine*, $OH\cdot CH_2\cdot CH_2\cdot NHPr^\beta$, boils at 171° under 741 mm. pressure, has a sp. gr. 0·8970 at 20°/4°, and n_D 1·4395 at 20°. The *hydrochloride*, *aurichloride*, and *platinichloride* are hygroscopic, and the last-named melts at about 85°; the *picrate* and *picrolonate* melt at 129° and 228° respectively.

*Hydroxyethyl*iso*butylamine*, $OH\cdot CH_2\cdot CH_2\cdot NH\cdot CH_2Pr^\beta$, boils at 190° under 756 mm. pressure, has a sp. gr. 0·8818 at 20°/4°, and n_D 1·4402 at 20°; the *picrate* and *picrolonate* melt at 115—117° and 232° respectively.

*Hydroxyethyl*iso*amylamine*, $OH\cdot CH_2\cdot CH_2\cdot NH\cdot CH_2\cdot CH_2Pr^\beta$, boils at 209—210° under 751 mm. pressure, has a specific gravity 0·8822 at 20°/4°, and n_D 1·4447 at 20°; the *hydrochloride* is exceedingly hygroscopic, whilst the *picrate* and *picrolonate* melt at 94—95° and 220° respectively.

Dihydroxydiethylamine, methyldihydroxydiethylamine, and ethyldihydroxydiethylamine have been already described (*loc. cit.*); the *picrolonate* of methyldihydroxydiethylamine crystallises from alcohol in lustrous, brownish-yellow prisms and melts at 164°.

Dihydroxydiethylpropylamine, $NPr^\alpha(CH_2\cdot CH_2\cdot OH)_2$, boils at 202—204° and 262—264° under 150 mm. and 753 mm. pressure respectively; it has a sp. gr. 0·9854 at 20°/4°, and n_D 1·4624 at 20°. The *picrate* and *picrolonate* melt at 85—90° and 126—128° respectively.

Dihydroxydiethylbutylamine, $C_4H_9\cdot N(CH_2\cdot CH_2\cdot OH)_2$, boils at 214° and 273—275° under 150 mm. and 741 mm. pressure respectively; it has a sp. gr. 0·9681 at 20°/4°, and n_D 1·4620 at 20°. The *picrate* and *picrolonate* melt at 88—95° and 135—136° respectively.

Dihydroxydiethylhexylamine, $C_6H_{13}\cdot N(CH_2\cdot CH_2\cdot OH)_2$, boils at 230—235° and 295—300° under 150 mm. and 751 mm. pressure respectively; it has a sp. gr. 0·9472 at 20°/4°, and n_D 1·4630 at 20°. The *picrolonate* melts at about 98°.

Dihydroxydiethylheptylamine, $C_7H_{15}\cdot N(CH_2\cdot CH_2\cdot OH)_2$, boils at 240—250° and 310—320° under 150 mm. and 751 mm. pressure respectively; it has a sp. gr. 0·9301 at 20°/4°, and n_D 1·4620.

*Dihydroxydiethyl*iso*propylamine*, $NPr^\beta(CH_2\cdot CH_2\cdot OH)_2$, boils at 200° and 261° under 150 mm. and 741 mm. pressure respectively; it has a sp. gr. 0·9859 at 20°/4°, and n_D 1·4620 at 20°. The *picrate* and *picrolonate* melt at 145° and 125° respectively.

*Dihydroxydiethyl*iso*butylamine*, $C_4H_9\cdot N(CH_2\cdot CH_2\cdot OH)_2$, boils at 202—204° and 264—265° under 150 mm. and 742 mm. pressure respectively; it has a sp. gr. 0·9534 at 20°/4°, and n_D 1·4561. The *picrolonate* melts at 113—114°.

*Dihydroxydiethyl*iso*amylamine*, $C_5H_{11}\cdot N(CH_2\cdot CH_2\cdot OH)_2$, boils at 216—219° and 278—281° under 150 mm. and 749 mm. pressure respectively; it has a sp. gr. 0·9516 at 20°/4°, and n_D 1·4598 at 20°. The *picrolonate* melts at 120—123°. M. O. F.

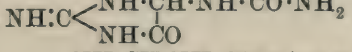
Alkylcyanomalonic Esters and their Corresponding Alkylcyanoacetic Acids. By ALBIN HALLER and GEORGES BLANC (*Compt. rend.*, 1901, **132**, 381—384. Compare Abstr., 1882, 1280).—The silver derivative of ethyl cyanomalonate, produced by treating the corresponding sodium compound with an aqueous solution of silver nitrate, reacts in its ketonic form when mixed with alkyl iodides dissolved in dry ether, giving rise to the corresponding cyanoalkylmalonic esters. The *ethyl* esters of cyanomethylmalonic, cyanoethylmalonic, and cyano-*n*-propylmalonic acids are mobile liquids having a faint odour and neutral reaction; they boil at 135°, 142—145°, and 155—157° respectively under pressures of 28—30 mm. When treated with boiling concentrated hydrochloric acid for 24 hours, these compounds are completely hydrolysed, with the formation of ammonium chloride, carbon dioxide, and the respective monocarboxylic derivatives, namely, propionic, butyric, and *n*-valeric acids. The addition of excess of 30 per cent. potassium hydroxide to these ethers brings about a vigorous reaction resulting in the formation of the corresponding cyanomonocarboxylic acids. These products were characterised by conversion into their calcium salts, and also by the formation of their anilides by the phenylcarbimide method (compare Abstr., 1896, i, 32). The anilides are sparingly soluble in water or light petroleum, but readily dissolve in alcohol.

a-Cyanopropionanilide, $CN\cdot CHMe\cdot CO\cdot NHPh$, *a-cyanobutyroanilide*, $CN\cdot CHEt\cdot CO\cdot NHPh$, and *a-cyanovaleranilide*, $CN\cdot CHPr^{\alpha}\cdot CO\cdot NHPh$, melt at 104—105°, 86—87°, and 88—89° respectively. G. T. M.

Compounds of Glyoxylic Acid with Guanidine and Aminoguanidine. By OSCAR DOEBNER and SIMON GÄRTNER (*Annalen*, 1901, **315**, 1—8).—Although glyoxylic acid unites with carbamide (2 mols.) to form allantoin, combination with guanidine proceeds on different lines. In a cold, aqueous solution, the guanidide of glyoxylic acid is produced, whilst at 100° ammonia is eliminated, and iminoallantoin is formed.

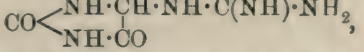
Guanidineglyoxylic acid, $NH_2\cdot C(NH)\cdot NH\cdot CH(OH)\cdot CO_2H$, prepared by adding guanidine carbonate to a 50 per cent. aqueous solution of glyoxylic acid until carbon dioxide is no longer liberated, crystallises from water in slender, colourless needles containing $\frac{1}{2}H_2O$, and melts at 210° to a brown liquid which evolves gas. The *ammonium* salt begins to turn brown at 198°, and melts, decomposing, at 225°. The *platinichloride* crystallises in yellow octahedra containing $1H_2O$.

Iminoallantoin,



$$NH{:}C\left\langle\begin{array}{l}NH\cdot\underset{|}{C}H\cdot NH\cdot CO\cdot NH_2\\ NH\cdot CO\end{array}\right.$$

or



$$CO\left\langle\begin{array}{l}NH\cdot\underset{|}{C}H\cdot NH\cdot C(NH)\cdot NH_2\\ NH\cdot CO\end{array}\right.,$$

obtained on adding guanidine carbonate (2 mols.) to a 15 per cent. solution of glyoxylic acid, and heating in a reflux apparatus during 20 minutes, crystallises from hot water, and sublimes at about 300° without undergoing fusion; the crystals contain $1H_2O$, which is removed at 130—140°. The *platinichloride* forms rhombic crystals containing $2H_2O$, and the *mercurichloride* crystallises in small white needles; the *aurichloride* is readily soluble in hot water, and crystallises in long, yellow prisms containing $2H_2O$.

Aminoguanidineglyoxylic acid, $NH_2\cdot C(NH)\cdot NH\cdot NH\cdot CH(OH)\cdot CO_2H$, produced from aminoguanidine acetate and glyoxylic acid, crystallises from hot water in aggregates of needles, and melts at 161°, when it decomposes. M. O. F.

Potassium and Sodium Thiocyanates and a Blue Colour produced by Heating Them. By WILLIAM B. GILES (*Chem. News*, 1901, **83**, 61—62).—When potassium thiocyanate or cyanide containing some, but not too much, sulphur, and no carbonate, is heated, a blue colour forms at a dull red heat, disappears on cooling, but reforms on reheating. D. A. L.

Presence of Guanine in Commercial Uric Acid. By LOUIS HUGOUNENQ (*J. Pharm.*, 1901, [vi], **13**, 167—169).—Commercial uric acid always contains guanine, which can be partly, but not entirely, removed by extraction with boiling dilute hydrochloric acid. The guanine may also be isolated by treatment of the commercial acid with an alkaline persulphate, whereby the uric acid is oxidised, while the guanine remains unacted on. H. R. LE S.

Asparagine and Aspartic Acid. By ADOLF JOLLES (*Ber.*, 1901, **34**, 386—390. Compare this vol., i, 30).—Aspartic acid, when oxidised with permanganate, gives a quantitative yield of ammonia, but no carbamide. Asparagine gives a 50 per cent. yield of carbamide, and 50 per cent. of ammonia. T. M. L.

Transformation of *iso*Dialuric Acid into Dialuric Acid. By PAUL KOECH (*Annalen*, 1901, **315**, 246—259).—It is well known that *iso*dialuric acid and carbamide undergo condensation to uric acid. An attempt to prepare iminouric acid from *iso*dialuric acid and guanidine resulted in the production of alloxantin, and this is now found to be due to the fact that, under the influence of bases, *iso*dialuric acid becomes transformed into dialuric acid. A description of the varying experimental conditions under which this change takes place constitutes the experimental portion of the paper. M. O. F.

Condensation of *iso*Dialuric Acid with Thiocarbamide. By CURT VON VOGEL (*Annalen*, 1901, **315**, 259—268).—The *compound*, $C_{16}H_{26}O_{11}N_{12}S_3$, prepared by heating *iso*dialuric acid with thiocarbamide and glacial acetic acid on a water-bath, crystallises in spherical aggregates of small, reddish-brown needles; it is practically insoluble in water, dilute acids, alcohol, and ether, but dissolves readily in sodium hydroxide and in concentrated sulphuric acid.

Boiling sodium hydroxide eliminates all the sulphur and a portion of the nitrogen from the substance, producing a sparingly soluble *sodium* salt, $C_{16}H_{17}O_{18}N_7Na_2$. The *compound*, $C_4H_5O_5N_3$, obtained by the action of concentrated nitric acid on the condensation product, crystallises in yellow needles; the *ammonium*, *sodium*, and *silver* salts are crystalline. M. O. F.

Action of Hydrofluosilicic Acid on Potassium Ferrocyanide. By J. MATUSCHEK (*Chem. Zeit.*, 1901, **25**, 158—159).—When solutions of potassium ferrocyanide and of hydrofluosilicic acid are mixed, a greenish coloration is produced, and if air is admitted a blue colour develops. This is a fairly delicate qualitative test. Experiments have shown that either in the cold or at 100° the products formed are Berlin blue and potassium silicofluoride. In the cold, a large excess of the acid is necesary, but at 100° the reaction may be represented by the equation $7H_4Fe(CN)_6 + 14H_2SiF_6 + O_2 = Fe_4(FeC_6N_6)_3 + 24HCN + 14K_2SiF_6 + H_2O$. J. J. S.

Mixed Organomagnesium Compounds. By VICTOR GRIGNARD (*Compt. rend.*, 1901, **132**, 558—561. Compare Abstr., 1900, i, 382; this vol., i, 250).—The product of the action of an alkyl iodide on magnesium in the presence of anhydrous ether may be either the compound $R\cdot MgI$ or a mixture of MgR_2 and magnesium iodide. Although the residue obtained on evaporating the ether has not been isolated in a state of purity, yet indirect evidence exists for believing the product to be $R\cdot MgI$. The substances are solid and not spontaneously inflammable in air, and are formed without any deposition of magnesium haloid salt. They react with aldehydes or ketones, giving rise to compounds containing the whole of the halogen present, and these products, when decomposed by water, yield secondary or tertiary alcohols without the evolution of any gaseous hydrocarbon. The *compound* from magnesium methiodide and acetone crystallises from ether and has the composition $CMe_3\cdot OMgI,Et_2O$.

The yield of alcohol obtained by this process always exceeds 50 per cent. of the theoretical. Similar results are obtained with the products of the interaction of magnesium and the alkyl bromides. The reaction between magnesium and the haloid ethers of unsaturated radicles takes a different course. When allyl bromide or iodide is employed, the product, being only slightly soluble in ether, is deposited, and, moreover, only half an atomic proportion of the metal is attacked by a mol. proportion of the organic compound. The *organomagnesium* compound produced crystallises in colourless, flattened needles, and has the composition C_3H_5MgI,C_3H_5I. The substance is very unstable, and does not readily react with aldehydes or ketones, the synthesis in this case being less efficient than that due to Saytzeff. G. T. M.

General Method for the Synthesis of Naphthenes. By PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1901, **132**, 566—568. Compare this vol., i, 210).—The property of hydrogenating benzene to *cyclo*hexane is peculiar to nickel; reduced cobalt and platinum black have a transitory action which is lost after a few minutes; spongy platinum or reduced iron and copper are quite inert. The reaction has been extended to the homologues of benzene and the following naphthenes, *o*- and *m*-dimethyl*cyclo*hexanes, and 1 : 3 : 5- and 1 : 2 : 4-trimethyl*cyclo*hexanes, have been prepared from the corresponding benzenoid hydrocarbons. *Ethyl*cyclo*hexane*, $C_6H_{11}Et$, boils at 128—129° (corr.), and has a sp. gr. 0·8026; *propyl*cyclo*hexane* boils at 153—154° (corr.) and has a sp. gr. 0·8098. A decanaphthene or menthane, $C_6H_{10}MePr^{\beta}$, boiling at 166—168° (corr.) is obtained from *p*-cymene. These naphthenes, when heated at 300° in the presence of reduced nickel, undergo decomposition, yielding methane, carbon, and the corresponding benzenoid hydrocarbon. G. T. M.

Organic Polysulphides and the Polysulphides of Sodium. By J. J. Blanksma (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, **3**, 457—459).—A continuation of earlier work (Abstr., 1900, i, 482). The di-, tri-, and tetra-sulphides of sodium exist as such in alcoholic solution, since they will react then with the nitro-derivatives of aromatic hydrocarbons forming aromatic di-, tri-, and tetra-sulphides. The aromatic tetrasulphides can also be obtained by treating the sodium derivatives of the disulphides with iodine, showing that the constitution of the tetrasulphides is $R\cdot S\cdot S\cdot S\cdot S\cdot R'$ and of sodium tetrasulphide $NaS\cdot S\cdot S\cdot SNa$. If sodium disulphide does not react with these nitro-compounds to form disulphides, it acts as a reducing agent, converting, for example, *m*-dinitrobenzene into *m*-*m*-dinitroazoxybenzene. R. H. P.

***p*-Toluenesulphinic Acid.** By Ernst von Meyer with R. Nacke and M. Gmeiner (*Chem. Centr.*, 1901, i, 455—456; from *Ber. k. sächs. Ges. Wiss. Math. phys. Cl.*, **52**, 124—139; *J. pr. Chem.*, 1901, [ii], **63**, 167—183).—p-*Tolylsulphonocarbinol*, $C_6H_4Me\cdot SO_2\cdot CH_2\cdot OH$, formed by heating formaldehyde with *p*-toluenesulphonic acid, crystallises from benzene in needles, melts at 90°, is easily soluble in alcohol, chloroform, or ether, and is resolved into its components by boiling water, dry ammonia, or sodium hydroxide solution; on oxidation it forms di-*p*-tolyldisulphone. The *acetate*, $C_6H_4Me\cdot SO_2\cdot CH_2\cdot OAc$, crystallises in prisms and melts at 78°; the *phosphate* crystallises in long plates and melts at 146°. *Di*-p-*tolylsulphonomethylamine*, $NH(CH_2\cdot SO_2\cdot C_6H_4Me)_2$, formed by dissolving the carbinol in ammonia and precipitating with hydrochloric acid, crystallises in long, slender needles, melts at 158—160° and is decomposed by hot sodium hydroxide solution. p-*Tolylsulphonocarbinylaniline*, $C_6H_4Me\cdot SO_2\cdot CH_2\cdot NHPh$, crystallises in slightly yellow, flat needles and melts at 137°. *Di*-p-*tolyldisulphone*, $C_{14}H_{14}O_4S_2$, formed by oxidising the carbinol with potassium permanganate dissolved in water or glacial acetic acid, crystallises from acetone in rhombohedra, decomposes at about 210° without melting, is almost insoluble in alcohol, ether, or benzene, and is quickly decomposed by alcoholic solutions of alkalis. By the action of alcoholic ammonia at 130°, ammonium *p*-toluenesulphinate and *p*-toluenesulphonamide are formed, but with phenylhydrazine it yields only phenylhydrazine *p*-toluenesulphinate.

Di-p-*tolylsulphonohydroxylamine*, $OH\cdot N(SO_2\cdot C_6H_4Me)_2$, prepared by adding solutions of sodium *p*-toluenesulphinate (2 mols.) and sodium nitrite (1 mol.) to cold dilute hydrochloric acid, crystallises from alcohol in needles, melts at 125°, and is decomposed by sodium hydroxide solution. The *benzoyl* derivative, $OBz\cdot N(SO_2\cdot C_6H_4Me)_2$, obtained by the action of benzoyl chloride on the preceding compound, crystallises from alcohol in rhombohedra and melts at 186°. *Tri*-p-*tolylsulphonamide*, $N(SO_2\cdot C_6H_4Me)_3$, formed by the action of nitrous acid on ditolylsulphonohydroxylamine dissolved in alcohol or in glacial acetic acid, or by the action of *p*-toluenesulphonic chloride dissolved in pyridine, or by treating ditolylsulphonohydroxylamine with *p*-toluenesulphinic acid in glacial acetic acid solution, crystallises in rhombic leaflets, melts at 184° and is slightly soluble in alcohol or glacial acetic acid.

p-*Tolylsulphonohydroxylamine*, $C_6H_4Me\cdot SO_2\cdot NH\cdot OH$, obtained by adding *p*-toluenesulphonic chloride to an alcoholic solution of hydroxylamine, crystallises from chloroform or benzene in matted needles, melts at 148°, is easily soluble in the ordinary solvents and is readily hydrolysed by aqueous solutions of alkalis. The *sodium* compound is thrown down as a white precipitate by sodium ethoxide. The *dibenzoyl* derivative, $C_6H_4Me\cdot SO_2\cdot NBz\cdot OBz$, crystallises in hexagonal plates and melts at 120°. When *p*-tolylsulphonohydroxylamine is treated with *p*-tolylsulphonic chloride in aqueous solution at 70°, di-*p*-tolyldisulphone is formed.

When aniline *p*-toluenesulphinate is gradually heated to 215° (compare Hälssig, Abstr., 1898, i, 141), it loses water, aniline, sulphur dioxide and traces of toluene, and from the blue mass which is formed, water extracts aniline *p*-toluenesulphonate. The residue when treated with dilute sulphuric acid yields the salt of a base which by the action of ammonia and ether is decomposed, forming p-*tolyl aminophenyl sulphide*, $C_6H_4Me\cdot S\cdot C_6H_4\cdot NH_2$; this crystallises from ether in flat needles, melts at 72°, is a feeble base and forms salts which are soluble in water. The *sulphate* crystallises in leaflets, the *hydrochloride* in long needles. The *methine* compound of p-*sulphotolylaniline*,

$$C_6H_4Me\cdot S\cdot C_6H_4\cdot NH\cdot CH{:}N\cdot C_6H_4S\cdot C_6H_4Me,$$

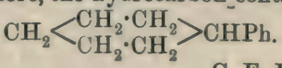
prepared by means of ethyl orthoformate, crystallises in needles. p-*Thiotolylanilinephenylthiocarbimide*,

$$C_6H_4Me\cdot S\cdot C_6H_4\cdot NH\cdot CS\cdot NHPh,$$

obtained by means of phenylthiocarbimide, crystallises in colourless needles and melts at 161°.

Tetramethylammonium *p*-toluenesulphinate decomposes above 180°, forming trimethylamine and methyl-*p*-tolylsulphone, $C_7H_7SO_2Me$, melting at 86°. The tetraethyl salt decomposes in a similar way, forming ethyl-*p*-tolylsulphone which melts at 57°. E. W. W.

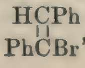
Formation of a Hydrocarbon, $C_{12}H_{16}$, from Quinitol. By Richard Willstätter and Rudolf Lessing (*Ber.*, 1901, **34**, 506—508).—When either the *cis*- or *trans*- form of quinitol (Baeyer, Abstr., 1894, i, 174) is heated with 60 per cent. sulphuric acid at 100°, a hydrocarbon, $C_{12}H_{16}$, is obtained which boils at 230—233° under 710 mm. pressure. It is stable to permanganate, but is attacked readily by bromine, hydrogen bromide being evolved; it can be nitrated with a mixture of nitric and sulphuric acids, and the nitro-derivative formed is reduced by tin and hydrochloric acid to an amine, which forms a crystalline hydrochloride, and can be diazotised and converted into azo-dyes. Probably, therefore, the hydrocarbon contains a benzene ring, and is *phenylcyclohexane*,



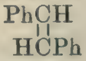
$CH_2{<}\begin{smallmatrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{smallmatrix}{>}CHPh$.

C. F. B.

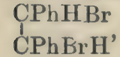
***iso*Stilbene.** By Johannes Wislicenus [and Moritz Jahrmarkt] (*Chem. Centr.*, 1901, i, 463—464, from *Ber. k. sächs. Ges. Wiss. Math. phys. Cl.*, 1900, **52**, 117—123. Compare Abstr., 1896, i, 98; 1897, i, 533).—Bromo*iso*stilbene,



$\begin{matrix}HCPh\\ \|\\ PhCBr\end{matrix}$, prepared by the action of potassium hydroxide on α-stilbene dibromide, crystallises in long, colourless needles, melts at 19°, and is not readily attacked by alcoholic potash. *iso*Stilbene,

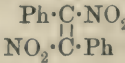


$\begin{array}{c}PhCH\\ \| \\ HCPh\end{array}$, obtained, together with stilbene, by reducing bromo*iso*stilbene with zinc dust and glacial acetic acid or alcohol, or with sodium amalgam and glacial acetic acid, is an oil which on distillation under atmospheric pressure is converted into ordinary stilbene, the boiling point rising from 270° to 300°, but it boils at 139—145° under 12 mm. pressure without change. It readily changes into stilbene on exposure to sunlight, or by the action of traces of bromine or iodine, and yields 83 per cent. of *iso*stilbene dibromide,

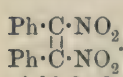


$\begin{array}{c}CPhHBr\\ | \\ CPhBrH\end{array}$, when it is dissolved in carbon disulphide and the solution added to cooled bromine in the dark. E. W. W.

The Two Stereoisomeric Diphenyldinitroethylenes (Dinitrostilbenes, Tolane Dinitrites). By JULIUS SCHMIDT (*Ber.*, 1901, **34**, 619—623).—When the gas evolved on warming arsenious oxide with concentrated nitric acid is passed into a cold ethereal solution of tolane, a mixture of nearly equal quantities of two *diphenyldinitroethylenes* (α and β) is obtained. The α-compound, being the less soluble, separates first, and crystallises from alcohol in bright yellow, lustrous needles, is not volatile with steam, and melts at 186—187°; the β-form crystallises from alcohol in lustrous, yellow pyramids and melts at 105—107°. Both compounds, in spite of their ethylenoid linking, fail to combine with bromine at 100°. Since the β-compound decomposes at 150°, whereas the α-compound is much more stable, the former probably has the configuration

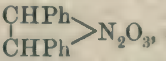


$\begin{array}{c}Ph{\cdot}C{\cdot}NO_2\\ \| \\ NO_2{\cdot}C{\cdot}Ph\end{array}$, and the latter,



$\begin{array}{c}Ph{\cdot}C{\cdot}NO_2\\ \| \\ Ph{\cdot}C{\cdot}NO_2\end{array}$. On reduction with zinc dust and acetic acid, both forms yield 2 : 3 : 5 : 6-tetraphenylpiperazine (this vol., i, 295). W. A. D.

Action of Nitrous Acid on Stilbene; s-Diphenyldinitroethane (Stilbene Dinitrite). By JULIUS SCHMIDT (*Ber.*, 1901, **34**, 623—626).—On passing the nitrous fumes evolved on warming arsenious oxide with nitric acid into a well cooled ethereal solution of stilbene, the *nitrosite*,



$\begin{array}{c}CHPh\\ | \\ CHPh\end{array}\!\!>N_2O_3$, separates in white crystals which soften at 160° and melt and decompose at 195—197°; the compound melting at 132° described by Angeli (Abstr., 1894, i, 75) could not be obtained. On dissolving the nitrosite in boiling glacial acetic acid, it is converted into s-α-*diphenyldinitroethane*, which crystallises in white, silky needles and melts and decomposes at 235—236°. Benzaldehyde was also formed (isolated as the phenylhydrazone) and a small quantity of a crystalline *substance* melting at 145—146°. W. A. D.

Compounds of Cupric Salts with Organic Bases. By DANIEL TOMBECK (*Ann. Chim. Phys.*, 1901, **22**, [vii], 113—144. Compare Abstr., 1898, i, 566; this vol., i, 135).—The *compound*,

$$Cu(C_2H_3O_2)_2,2NH_2Ph,H_2O,$$

produced by adding aniline to an aqueous solution of copper acetate placed in an inert atmosphere, separates from solution in small, dark green needles, which rapidly turn brown on exposure to air; it dissolves in water or alcohol, the aqueous solution rapidly decomposing, especially on raising the temperature.

The *double* salt, $Cu(C_2H_3O_2)_2,2NH_3Ph{\cdot}C_2H_3O_2,H_2O$, formed by acidifying the solution of the preceding compound with acetic acid, crystallises in light green, silky needles soluble in water or alcohol without decomposition and melting in its own water of crystallisation.

The *compound*, $Cu(HCO_2)_2,2NH_2Ph$, resembles the corresponding acetate, and is formed by adding powdered copper formate to aniline, the corresponding *oxalate*, $CuC_2O_4,2NH_2Ph$, being obtained in a similar manner.

The *compound*, $CuSO_4,4C_5NH_5$, is a dark blue, amorphous powder, produced when anhydrous copper sulphate is placed in a dry atmosphere containing pyridine vapour; the hydrated form of this substance crystallises with $4H_2O$, and is obtained by adding pyridine to a saturated solution of copper sulphate. The *double* salt,

$$CuSO_4,2(C_5NH_5,H_2SO_4),6H_2O,$$

is formed by adding sulphuric acid to the aqueous solution of the preceding compound until its colour changes from blue to green; it separates in blue, prismatic crystals soluble in water or dilute sulphuric acid, the solution in the latter case being almost colourless. The *nitrate*, $Cu(NO_3)_2,4C_5NH_5,6H_2O$, crystallises in large, indigo-blue prisms, and loses pyridine at the ordinary temperature, passing into the *compound* $Cu(NO_3)_2,2C_5NH_5,4H_2O$.

With the acetate, formate, and oxalate of copper, pyridine forms the following *compounds* respectively: $Cu(C_2H_3O_2)_2,4C_5NH_5$; $Cu(HCO_2)_2,4C_5NH_5,4H_2O$, and $CuC_2O_4,4C_5NH_5,2H_2O$; the *double acetate*, $Cu(C_2H_3O_2)_2,2(C_5NH_5,C_2H_4O_2),2H_2O$, being produced by the action of acetic acid on a solution of the first of these substances.

The *compound*, $CuCl_2,2C_6H_7N,2H_2O$, obtained in light blue needles when an alcoholic solution of cupric chloride is treated with picoline, dissolves in this base, giving rise to a second *derivative*,

$$CuCl_2,4C_6H_7N,2H_2O.$$

The *double* salt, $CuCl_2,2(C_6H_7N,HCl),2H_2O$, produced by adding dilute hydrochloric acid to solutions of the preceding compounds, forms reddish-yellow crystals soluble in water or alcohol. Anhydrous copper sulphate absorbs the vapour of picoline, yielding the compound $CuSO_4,4C_6H_7N$, the *hydrated* derivative, $CuSO_4,2C_6H_7N,5H_2O$, being produced by the addition of the base to a saturated solution of the copper salt.

The following *compounds* are obtained respectively from picoline and copper nitrate, oxalate, or acetate: $Cu(NO_3)_2,4C_6H_7N,6H_2O$, $Cu(NO_3)_2,2C_6H_7N,4H_2O$, $CuC_2O_4,4C_6H_7N,2H_2O$, and

$$Cu(C_2H_3O_2)_2,4C_6H_7N,2H_2O.$$

The *compounds* of the copper salts with α-lutidine resemble those of its lower homologue, and are produced by similar methods; the following have been prepared: $CuCl_2,2C_7H_9N,2H_2O$, $CuCl_2,4C_7H_9N,2H_2O$, $CuSO_4,4C_7H_9N$, $CuSO_4,2C_7H_9N,5H_2O$, $Cu(NO_3)_2,4C_7H_9N,6H_2O$, $CuC_2O_4,2C_7H_9N,2H_2O$.

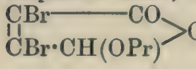
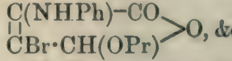
G. T. M.

A New Method of Preparing *p*-Alkyloxybenzylanilines and their Homologues. By PAUL FRITSCH (*Annalen*, 1901, **315**, 138—143).—When anhydroformaldehydeaniline is added slowly to a mixture of a phenol ether and sulphuric acid, the corresponding *p*-alkyloxybenzylaniline is produced, the best yield being obtained with 83·5 per cent. acid. By this method the author has prepared *p*-methoxybenzylaniline, *p*-ethoxybenzylaniline, *p*-methoxybenzyl-*o*-toluidine and *p*-ethoxybenzyl-*o*-toluidine; they melt at 64·5°, 65°, 55°, and 53° respectively.

M. O. F.

Action of Primary Amines on Mucobromic and Mucochloric Acids and their Esters. By HUGO SIMONIS (*Ber.*, 1901, **34**, 509—519).—Mucobromic and mucochloric acids, $CHO\cdot CBr\colon CBr\cdot CO_2H$, &c. (Abstr., 1899, i, 741), react vigorously with aniline or *p*-toluidine in the presence of a little absolute alcohol, mucochloric acid especially so; a freezing mixture must be employed to moderate the violence of the action. With 1 mol. of the base, NH_2Pb, &c., substituted iminomucobromic acids, $NPh\colon CH\cdot CBr\colon CBr\cdot CO_2H$, &c., are formed; with 2 mols. substituted aminoiminomucobromic acids,

$$NPh\colon CH\cdot CBr\colon C(NHPh)\cdot CO_2H,$$

which are yellow, and lose carbon dioxide when heated, forming substituted α-bromo-β-aminoiminoacraldehyde, $NPh\colon CH\cdot CBr\colon CH\cdot NHPh$; with an excess of the base, preferably 5—6 mols., the aniline salt of the last acid, $NPh\colon CH\cdot CBr\colon C(NHPh)\cdot CO_2\cdot NH_3Ph$, which is yellow, and is decomposed into the acid and aniline by water. Various esters of mucobromic and mucochloric acids were prepared by boiling the acids for 2 hours with excess of the alcohol and a few drops of strong sulphuric acid; they appear to be ψ-esters, with the constitution  $\left.\begin{array}{l}CBr\text{———}CO\\ \ \|\\ CBr\cdot CH(OPr)\end{array}\right\rangle O$, for they only react with 1 mol. of aniline or *p*-toluidine, forming phenylaminomucobromates,  $\left.\begin{array}{l}C(NHPh)\text{—}CO\\ \ \|\\ CBr\cdot CH(OPr)\end{array}\right\rangle O$, &c. The compounds prepared are enumerated below, with the temperatures at which they decompose (or melt, when that is stated expressly).

Phenyliminomucobromic acid, 126°; *phenyliminophenylaminomucobromic acid*, 135—140°, its *silver* salt and yellow mono*benzoyl* derivative melting at 103—105°, and *aniline* salt; also *α-bromo-β-phenylaminophenyliminoacraldehyde*, 144—146°; *phenyliminomucochloric acid*, 132°; *phenyliminophenylaminomucochloric acid*, 150°; *p-tolylimino*-p-*tolylaminomucobromic acid*, 165—168°.

Propyl and *allyl mucobromates*, melting at 31·5° and 41° respectively; *methyl*, *ethyl*, *propyl*, and *allyl mucochlorates*, all liquid; *methyl*, *ethyl*, and *propyl phenylaminomucobromates*, melting at 117°, 114°, and 80° respectively; *methyl mucochlorate*, crystalline; *methyl*-p-*tolylaminomucochlorate*, melting at 118°; *ethyl*-m-*xylylaminomucochlorate*, melting at 114°.

C. F. B.

New Colouring Matters. By EDOUARD GRIMAUX and LÉON LEFÈVRE (*Bull. Soc. Chim.*, 1901, [iii], **25**, 213—214).—Various azo-colouring matters, details of which are not given in the paper, are obtained by the action of phenols, naphthols, amines, &c., on the products of diazotisation of derivatives of triphenylmethane and its homologues. Monoamines, diamines, and triamines have been experimented with.

Colouring matters of the resaurine and resoxeine classes are obtained (1) by the action of sulphuric acid on resorcinol at 100°; (2) by the action of nitric and sulphuric acids on resorcinol; (3) by brominating the latter derivative; (4) by the action of aniline on resoxeine at 150°; (5) by the alkylation of resoxeine and of Nencki's resaurine; (6) by brominating the preceding; (7) by brominating resaurine; (8) by the action of aniline on resaurine at 150°. N. L.

Blue Colouring Matters derived from Triphenylmethane. By Edouard Grimaux (*Bull. Soc. Chim.*, 1901, [iii], **25**, 215).—The action of carbonyl chloride on *m*-dimethylaminomethoxybenzene and its homologues in the presence of aluminium chloride results in the formation of soluble, blue colouring matters of the type

$$CCl[C_6H_3(OEt)\cdot NMe_2]_3.$$

N. L.

Red Colouring Matters derived from Triphenylmethane. By Edouard Grimaux (*Bull. Soc. Chim.*, 1901, [iii], **25**, 215—216).—Fluorescent, red colouring matters are obtained by heating *m*-dimethylaminomethoxybenzene or its homologues with phthalic anhydride at 175—180°. N. L.

Derivatives of Triphenylmethane. By Edouard Grimaux (*Bull. Soc. Chim.*, 1901, [iii], **25**, 216—217).—A blue colouring matter is formed by the oxidation of *o*-dimethylaminomethoxybenzene or its next higher homologue. The red colouring matter obtained by the action of phthalic anhydride on *m*-dimethylaminomethoxybenzene or its homologues (preceding abstract) is converted by the action of sulphuric acid into a new colouring matter of a less violet tint. Substituted rhodamines behave in a similar manner. When treated with carbon tetrachloride, *o*-dimethylaminomethoxybenzene yields a colourless compound which furnishes a violet colouring matter on oxidation with lead peroxide. *m*-Dimethylaminoethoxybenzene forms a garnet-coloured dye when treated with arsenic acid at 180—185°. N. L.

Preparation of *m*-Alkylaminophenols. By Edouard Grimaux (*Bull. Soc. Chim.*, 1901, [iii], **25**, 217—218).—*m*-Dimethylaminophenol and *m*-diethylaminophenol are obtained by heating dimethylamine and diethylamine respectively with resorcinol at 200°. When heated with dimethylamine or diethylamine at 200—255°, fluorescein yields colouring matters resembling the rhodamines. A green colouring matter resembling malachite-green is obtained by oxidising the product of the condensation of dimethylaminomethoxybenzene or its homologues with benzaldehyde or nitrobenzaldehyde. N. L.

Colouring Matters derived from *m*-Dialkylaminoalkyloxybenzenes. By Edouard Grimaux (*Bull. Soc. Chim.*, 1901, [iii], **25**, 219—220).—The hydrochloride of 4-nitroso-1-dimethylamino-3-ethoxybenzene yields (1) an ethoxyindophenol when reduced with zinc dust and subsequently oxidised with potassium dichromate in presence of α-naphthol; (2) an ethoxytolylene-blue when heated with *m*-tolylenediamine; (3) a blue colouring matter, an ethoxy-derivative of

Meldola's blue, by heating with β-naphthol in acetic acid solution; (4) safranines, when heated with zinc dust and subsequently oxidised in presence of primary amines; (5) an ethoxylated gallocyanin when boiled with tannin; (6) a blue colouring matter when heated with resorcinol; (7) a blue colouring matter when reduced with zinc dust and treated with *m*-dimethylaminophenol in alkaline solution.

N. L.

Action of Aromatic Sulphonic Chlorides on Carbamide. By Ira Remsen and W. W. Garner (*Amer. Chem. J.*, 1901, **25**, 173—190).—The condensation product obtained by heating carbamide, $2CO(NH_2)_2$, with a sulphonic chloride, $R{\cdot}SO_2Cl$ (compare Elander, Abstr., 1881, 164), is shown to be a *guanylcarbamide sulphonate*,

$$NH_2{\cdot}CO{\cdot}N{:}C(NH_2)_2,R{\cdot}SO_3H.$$

These can be synthesised from guanylcarbamide and the sulphonic acids, and yield, as a precipitate, the pink copper derivative of guanylcarbamide when heated with sodium hydroxide and copper sulphate. From this copper derivative, guanylcarbamide itself can be obtained, and indeed this new method of preparing it is the best available at present. These guanylcarbamide sulphonates evolve carbon dioxide and ammonia, and form *guanidine sulphonates*,

$$NH{:}C(NH_2)_2,R{\cdot}SO_3H,$$

(identical with products synthesised from guanidine carbonate and the sulphonic acids), when they are heated with dilute hydrochloric acid at 170—180°; with fuming nitric acid, they yield nitroguanidine; when boiled with aqueous potassium carbonate, they yield ammonia, carbon dioxide, and guanidine sulphonates, and when boiled with aqueous barium hydroxide they yield ammonia, barium carbonate, and barium sulphonates.

In the case of *p*-toluenesulphonic chloride, its action on carbamide was also tried in alcoholic solution; the product was carbamide *p*-toluenesulphonate.

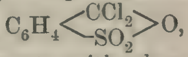
The following substances were prepared; the numbers are melting points: *Guanylcarbamide benzenesulphonate*, 216°; p-*toluenesulphonate*, 224°; o-*toluenesulphonate*, 205°; *a-naphthalenesulphonate*, 223°; *β-naphthalenesulphonate*, 237°. *Guanidine benzenesulphonate*, 206°; p-*toluenesulphonate*, 206°; *a-naphthalenesulphonate*; *β-naphthalenesulphonate*, 259°.

C. F. B.

Action of Aromatic Sulphonic Chlorides on Thiocarbamide. By Ira Remsen and H. J. Turner (*Amer. Chem. J.*, 1901, **25**, 190—202).—When a sulphonic chloride, $R{\cdot}SO_2Cl$, is warmed with thiocarbamide, $CS(NH_2)_2$, in alcoholic solution, needles of dithiocarbamide dichloride, $CCl(NH_2)_2{\cdot}S{\cdot}S{\cdot}CCl(NH_2)_2$, separate (the yield can be increased by diluting with ether), whilst a disulphoxide, $SRO{\cdot}SRO$ (or thiosulphonate, $R{\cdot}SO_2{\cdot}SR$) remains in solution and can be precipitated by diluting with water; sulphur is also formed. Apparently these disulphoxides are best prepared in this way. The reaction was carried out in the case of the benzene and *p*-toluene derivatives.

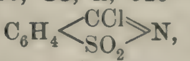
With ammonium thiocyanate, benzenesulphonic chloride yields no well characterised product.

From potassium benzene- or *p*-toluene-sulphinate and dithiocarbamide dichloride in alcoholic solution, the disulphoxide is obtained, along with another crystalline product, free from nitrogen. The product melted at 99·5° and 155—158° in the two cases respectively. A hydrosulphide and sulphur are also formed. C. F. B.

Action of the Chlorides of *o*-Sulphobenzoic and of *p*-Nitro-*o*-sulphobenzoic Acids on Carbamide. By WILLIS B. HOLMES (*Amer. Chem. J.*, 1901, **25**, 202—216).—Symmetrical (stable) *o*-sulphobenzoic chloride, $COCl\cdot C_6H_4\cdot SO_2Cl$, is obtained best by dissolving the mixture of isomeric chlorides (Remsen, Abstr., 1895, i, 472; List and Stein, Abstr., 1898, i, 584) in ether and shaking with ammonia, which is added gradually until its odour is just perceptible after shaking. The unsymmetrical (labile) chloride,  $C_6H_4<\genfrac{}{}{0pt}{}{CCl_2}{SO_2}>O$, is obtained best by heating potassium *o*-sulphobenzoate with phosphorus oxychloride at 135°; it melts at 40°, not at 21°. A mixture of the two chlorides crystallises like a homogeneous substance, and has melting point 21°.

When either of these two chlorides is heated at 100° with carbamide (1 : 4 mols.) for several days, a product is obtained that could not be isolated but yielded ammonium benzoylcarbamide-*o*-sulphonate, $NH_2\cdot CO\cdot NH\cdot CO\cdot C_6H_4\cdot SO_3NH_4$, when dissolved in water. This salt is converted by cold aqueous barium hydroxide into the barium salt; boiling dilute aqueous potassium hydroxide eliminates ammonia and carbon dioxide, and forms the potassium salt of *o*-benzaminosulphonic acid, $NH_2\cdot CO\cdot C_6H_4\cdot SO_3K$; boiling dilute hydrochloric acid hydrolyses it to *o*-sulphobenzoic acid. The same product is obtained from both chlorides, and in the same yield, namely 55 per cent. of the theoretical. From the isomeric *p*-nitro-*o*-sulphobenzoic chlorides, analogous derivatives were obtained. The substances prepared are enumerated below, with their melting points and water of crystallisation.

*Benzoylcarbamide-*o*-sulphonic acid*, crystalline, very soluble in water; *ammonium*, 266°, *barium* $BaA_2,2H_2O$, *potassium*, 286°, sodium, NaA,H_2O, *lead*, $PbA_2,3H_2O$, *copper*, $CuA_2,6H_2O$, and *silver* salts. p-*Nitrobenzoylcarbamide-*o*-sulphonic acid*, very soluble; its *ammonium*, 273°, *barium*, $BaA_2,2H_2O$, *potassium*, KA,H_2O, *sodium*, NaA,H_2O or $4H_2O$, *lead*, $PbA_2,5H_2O$, *copper*, $CuA_2,3H_2O$, and *silver* salts [$A = NH_2\cdot CO\cdot NH\cdot CO\cdot C_6H_4\cdot SO_3\cdot$ and $NH_2\cdot CO\cdot NH\cdot C_6H_3(NO_2)\cdot SO_3\cdot$ respectively]. C. F. B.

Chloro-derivatives of *o*-Benzoicsulphinide. By C. MASELLI (*Gazzetta*, 1900, **30**, ii, 529—539).—*Chlorobenzalsultim* ("chloro-ψ-saccharin"),  $C_6H_4<\genfrac{}{}{0pt}{}{CCl}{SO_2}>N$, prepared by passing chlorine into an aqueous solution of *o*-benzoicsulphinide, is slightly soluble in chloroform, carbon tetrachloride, benzene, or *p*-xylene, more so in light petroleum or toluene, and separates from the last-named solvent in white crystals melting at about 170°. When heated at 190° in an atmosphere of carbon dioxide, it sublimes in long acicular crystals with partial decomposition. It has the normal molecular weight in freezing acetic acid, and by the action of alcohol is converted into ethoxybenzalsultim ("ethoxy-ψ-saccharin"). T. H. P.

Preparation of Anils [Phenylimides] of Acid Cyanides. By FRANZ SACHS [and in part EDUARD BRY and C. MEREDITH WHITTAKER] (*Ber.*, 1901, **34**, 494—503).—Substituted aromatic aminobenzyl cyanides, $CN\cdot CHPh\cdot NHR$, can be obtained by heating benzaldehyde cyanohydrin, $CN\cdot CHPh\cdot OH$, with an aromatic amine, NH_2R, and a little alcohol at 100° (Tiemann and Piest, Abstr., 1883, 198). They can be oxidised in boiling acetone solution by potassium permanganate to yellow substituted iminobenzoyl cyanides, $CN\cdot CPh{:}NR$; when $R = C_6H_4\cdot NMe_2$, the oxidation can even be effected by aspirating air through the boiling solution of the base. (This action of permanganate on the saturated grouping $>CH\cdot NH\cdot$, which it converts readily into the unsaturated one, $>C{:}N\cdot$, is in strong contrast to its action on the typical unsaturated hydrocarbon grouping; in the latter case, an unsaturated grouping, $>C{:}C<$, is converted into a saturated one, $>C(OH)\cdot C(OH)<$, &c.) The same iminobenzoyl cyanides are obtained by heating benzyl cyanide with an aromatic nitroso-derivative to boiling in alcoholic solution, and adding a little sodium carbonate solution; so obtained, however, they sometimes differ slightly from those obtained by the first method, and possibly are stereoisomeric with them. They can be reduced by zinc and ammonium or calcium chloride in alcoholic or acetone solution, but it is difficult satisfactorily to isolate the products.

Phenyliminobenzoyl cyanide, $R = Ph$, when made by the first method, melts at 72° and is not hydrolysed by sulphuric acid; when made by the second method it contains $\frac{3}{4}$ H_2O in addition, melts at 135°, and is converted into *phenyliminobenzoylformamide*, $NH_2\cdot CO\cdot CPh{:}NPh$, melting at 141°, when it is dissolved in strong, cold sulphuric acid and the solution poured into water. p-*Tolyliminobenzoyl cyanide*, $R = CH_2Ph$, melts at 96° when made by the first method; when made by the second method, it contains $\frac{1}{4}H_2O$ in addition, and melts at 93—94°. o-*Tolyliminobenzoyl cyanide* has the same composition when made by either method, and melts at 85°; o-*tolylaminobenzyl cyanide* melts at 71°. *p*-Dimethylaminophenyliminobenzoyl cyanide, $R = C_6H_4\cdot NMe_2$ (4-dimethylamidophenyl-μ-cyanazomethinephenyl, Abstr., 1899, i, 884) was obtained by the first method from p-*dimethylaminophenylaminobenzyl cyanide*, which is red, and melts at 104°. *Phenylimino*-p-*nitrobenzoyl cyanide*, $CN\cdot C(C_6H_4\cdot NO_2){:}NPh$, was obtained by the second method from *p*-nitrobenzyl cyanide; it is yellow, and melts at 130°; the homologous p- and o-*tolyl* compounds are orange coloured, and both melt at 121—122°.

C. F. B.

An Isomeride of Anethole and the Constitution of the latter Compound. By AUGUSTE BÉHAL and TIFFENEAU (*Compt. rend.*, 1901, **132**, 561—563).—p-ψ-*Propenylanisole*,

$$OMe\cdot C_6H_4\cdot CMe{:}CH_2,$$

and a bimolecular substance are produced simultaneously by the condensation of ethyl anisate with magnesium methiodide, the two substances being separated by distilling the product in steam, when the former distils over, whilst the polymeride remains in the residue.

p-ψ-Propenylanisole melts at 32° and boils at 222° under the ordinary pressure; it dissolves in alcohol, but is almost insoluble in water, and has an odour intermediate between those of anethole and estragole. The polymeride crystallises from absolute alcohol in aggregates of needles melting at 58°, and distils without alteration in a vacuum; when heated under the ordinary pressure, the temperature rises to 350° and then falls, a volatile product being obtained which, when rectified, distils at 215—230° and yields, on cooling, crystals of the unimolecular substance melting at 32° and boiling at 222°. The bimolecular substance does not combine additively with bromine, a fact which indicates that the ethylene linking is involved in the polymeric change.

Anethole and its polymeride are produced by the action of magnesium ethiodide, this synthesis indicating that the unimolecular compound contains a propenylic chain, and possesses the constitution represented by the formula $OMe\cdot C_6H_4\cdot CH\colon CHMe$. Bougault (Abstr., 1900, i, 495) showed that the aldehyde formed from anethole by the action of iodine and mercuric oxide in the presence of alcohol has the constitution $OMe\cdot C_6H_4\cdot CHMe\cdot CHO$. It follows that this condensation has been accompanied by a change of the propenylic chain into an *iso*propyl grouping. A similar transformation is observed on treating *p-ψ*-propenylanisole in a like manner, the product being a *ketone*, to which the constitution $OMe\cdot C_6H_4\cdot CH_2\cdot COMe$ is given for the following reasons. The new compound boils at 264°, whilst Bougault's isomeric aldehyde boils at 255°; it yields an unstable sodium hydrogen sulphite compound, and an oxime crystallising in fasciculated needles melting at 72°. The ketonic nature of the substance is further demonstrated by the fact that it does not yield an acid on treatment with oxidising agents or alcoholic potassium hydroxide. It does not develop a coloration with a sulphurous acid solution of magenta, and is decomposed by alkali hypobromites into bromoform and anisic acid. G. T. M.

Aromatic Tellurium Compounds. By E. ROHRBAECH (*Annalen*, 1901, **315**, 9—18. Compare Rust, Abstr., 1898, i, 137).—p-*Telluroanisole*, $Te(C_6H_4\cdot OMe)_2$, obtained from dichlorotelluroanisole (*loc. cit.*) by the action of zinc dust on a boiling solution in benzene, separates from dilute alcohol in lustrous, reddish-brown crystals and melts at 50°; chlorine regenerates dichlorotelluroanisole, and bromine gives rise to the dibromide. Telluroanisole dissolves in hot dilute nitric acid, becoming converted into the dinitrate, which melts at 126° (*loc. cit.*).

p-*Tellurophenetole*, $Te(C_6H_4\cdot OEt)_2$, prepared from dichlorotellurophenetole, crystallises in yellow plates and melts at 64°. The position occupied by the tellurium is indicated by the fact that when dichlorotellurophenetole is heated in a sealed tube at 200° it is resolved into tellurium and *p*-chlorophenetole.

Attempts to prepare a thio-compound corresponding to tellurophenetole by the action of tellurium tetrachloride on thiophenetole were unsuccessful; either no change occurred, or the action was so vigorous that tellurium was precipitated. Tellurium tetrachloride and thiophenol give phenyl disulphide, tellurium, and hydrogen chloride.

Ditelluroanisyl trisulphide, $S(TeS\cdot C_6H_4\cdot OMe)_2$, prepared by the action of colourless ammonium hydrogen sulphide on dichlorotelluroanisole in alcohol, crystallises from alcohol in small, dark red needles and melts at 61°. *Ditellurophenetyl trisulphide*, $S(TeS\cdot C_6H_4\cdot OEt)_2$, crystallises from alcohol in small, reddish-brown needles and melts at 114°. *Ditellurophenetyl pentasulphide*, $S(TeS_2\cdot C_6H_4\cdot OEt)_2$, obtained from dichlorotellurophenetole and yellow ammonium sulphide, crystallises from alcohol in silky, reddish-brown needles and melts at 92°.

Dichlorotelluromethyl p-*phenetyl ketone*, $TeCl_2\cdot(CH_2\cdot CO\cdot C_6H_4\cdot OEt)_2$, produced by the action of tellurium tetrachloride on *p*-phenetyl methyl ketone in ether, crystallises from a mixture of ether and chloroform in small, white needles, which become black at 184° and melt, evolving gas, at 212—213°.

Dichlorotelluromethyl m-*xylyl ketone*, $TeCl_2(CH_2\cdot CO\cdot C_6H_3Me_2)_2$, crystallises in small, lustrous needles and melts at 180°. *Dichlorotelluromethyl ψ-cumyl ketone*, $TeCl_2(CH_2\cdot CO\cdot C_6H_2Me_3)_2$, also forms white needles and melts at 188°. *Dichlorotelluroacetocumene*,

$$TeCl_2(CH_2\cdot CO\cdot C_6H_4,Pr^{\beta})_2,$$

melts at 183°.

Dichlorotelluromethyl α-naphthyl ketone, $TeCl_2(CH_2\cdot CO\cdot C_{10}H_{17})_2$, prepared from tellurium tetrachloride and α-naphthyl methyl ketone, crystallises from chloroform and melts at 203—204°. M. O. F.

Pyrogallolsulphonic Acids. By MARCEL DELAGE (*Compt. rend.*, 1901, **132**, 421—423).—*Pyrogalloldisulphonic acid*,

$$C_6H(OH)_3(SO_3H)_2,4H_2O,$$

is obtained in the form of felted, hygroscopic needles by treating pyrogallol with ordinary concentrated sulphuric acid as in the preparation of the monosulphonic acid (compare Abstr., 1900, i, 595), adding to the product fuming sulphuric acid, subsequently diluting the mixture with water, and allowing the solution to crystallise in a dry atmosphere. When the crystals are kept in a desiccator over sulphuric acid they effloresce, losing $2H_2O$.

Barium pyrogalloldisulphonate, $C_6H(OH)_3(SO_3)_2Ba,\frac{1}{2}H_2O$, separates in well-defined, light yellow crystals; the *calcium* salt is obtained as a pale, yellowish-white, crystalline powder containing $4H_2O$, and losing this by efflorescence on exposure to air; it is less stable than the barium compound, being partially decomposed by repeated crystallisation.

G. T. M.

3 : 4 : 3′ : 4′-Tetramethoxystilbene. By W. FEUERSTEIN (*Ber.*, 1901, **34**, 415—416).—Veratrole readily condenses with chloral hydrate in a similar manner to other phenol ethers (Elbs, Abstr., 1893, i, 271) to form *tetramethoxydiphenyltrichloroethane*, which is readily reduced by zinc dust to *tetramethoxystilbene*, $C_6H_3(OMe)_2\cdot CH{:}CH\cdot C_6H_3(OMe)_2$; this crystallises in plates possessing a strong violet fluorescence and melting at 155—156°. A. H.

Phenylmethylallylcarbinol. By ALEXANDER ARBUSOF (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 38—45).—*Phenylmethylallylcarbinol*, $C_3H_5\cdot CMePh\cdot OH$, obtained by the action of zinc or magnesium on acetophenone and allyl iodide in ethereal solution, is a mobile, highly refractive liquid, insoluble in water, and boiling at 217—223° (uncorr.); it has the sp. gr. 0·99934 at 20°/0° and 1·00040 at 20°/20°. When gently oxidised with potassium permanganate solution, it yields the *trihydric alcohol* of the constitution $OH\cdot CMePh\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$, in the form of a syrupy liquid readily soluble in water, alcohol, or ether, whilst more energetic oxidation gives *β-phenylmethylhydracrylic acid*, $C_{10}H_{12}O_3$, forming stellate aggregates of acicular crystals melting at 50—53°; the *calcium*, with $2\frac{1}{2}H_2O$, *silver* and *zinc*, with $2H_2O$, salts of the acid were analysed. T. H. P.

Derivatives of Helicin. By EMIL FISCHER (*Ber.*, 1901, **34**, 629—631).—*Helicin cyanhydrin*, $CN\cdot CH(OH)\cdot C_6H_4\cdot O\cdot C_6H_{11}O_5$, prepared by the action of hydrogen cyanide on an aqueous solution of helicin, crystallises from hot water in square tablets, melts and decomposes at 176°, and dissolves readily in warm alcohol or water, but on boiling the solution is rapidly decomposed into helicin and hydrogen cyanide, and could not therefore be hydrolysed to the acid or to dextrose and salicylaldehyde cyanohydrin.

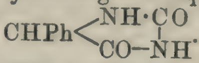
a-Phenyl-o-glucocoumaronitrile, $CN\cdot CPh\colon CH\cdot C_6H_4\cdot O\cdot C_6H_{11}O_5$, prepared by condensing helicin with benzyl cyanide, crystallises from dilute alcohol in minute, felted needles and melts at 175—176°.

T. M. L.

Nitration of *o*-Chloro- and *o*-Bromo-benzoic Acids. By ARNOLD F. HOLLEMANN (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, **3**, 462—463).—*2-Chloro-3-nitrobenzoic acid*, which melts at 185°, has been separated by the fractional crystallisation of the potassium salts from the 2 : 5-acid, which is the principal product of the nitration of *o*-chlorobenzoic acid (Abstr., 1900, i, 388). *2-Bromo-3-nitrobenzoic acid* melts at 191°, and is obtained in a similar manner to the analogous chloro-acid.

R. H. P.

Condensation of Benzaldehydecyanohydrin with Urethane. By FRITZ LEHMANN (*Ber.*, 1901, **34**, 366—377).—By heating together mol. proportions of benzaldehyde and urethane, Bischoff's benzylidenediurethane (Abstr., 1874, 890) is produced, but in presence of zinc chloride the product is *urethanophenylacetonitrile*, $CN\cdot CHPh\cdot NH\cdot CO_2Et$, which crystallises from light petroleum, melts at 83°, is not acted on by acetic anhydride, and does not dissolve in dilute acids or alkalis, but is converted into the amide by concentrated sulphuric or hydrochloric acid. *Urethanophenylacetamide*, $NH_2\cdot CO\cdot CHPh\cdot NH\cdot CO_2Et$, crystallises from alcohol in four-sided prisms, melts at 206—207° (corr.), dissolves in cold sulphuric and hydrochloric acids, is precipitated unchanged on dilution, and is converted by heating with aqueous potassium hydroxide into a-phenylhydantoin,



$CHPh<\begin{matrix}NH\cdot CO\\ CO-NH\end{matrix}$.

By passing hydrogen chloride into a hot alcoholic solution of the nitrile or amide, ethyl urethanophenylacetate, $CO_2Et\cdot CHPh\cdot NH\cdot CO_2Et$, is produced (Kossel, Abstr., 1892, 468), and from this the acid can be prepared by hydrolysing with potassium hydroxide, but melts at 119—121° (corr.), and not at 155° as stated by Kossel. *Urethanophenylacetoxamidine*, $CO_2Et\cdot NH\cdot CHPh\cdot C(NH)\cdot NH\cdot OH$, prepared by the action of hydroxylamine on the nitrile, crystallises from hot water in small prisms, sinters at 133°, and melts at 137° (corr.), forms a crystalline hydrochloride and hydrobromide, but has no basic properties and does not dissolve in cold dilute potassium or sodium hydroxide, but is decomposed, with liberation of hydroxylamine, when the mixture is heated; the *acetyl* derivative, $C_{13}H_{17}O_4N_3$, crystallises from alcohol and melts at 162°; the oxamidine combines with cyanic acid to a *compound*, $C_{12}H_{16}O_4N_4$, which melts and liberates gas at 160°, has feeble basic properties, and forms a crystalline nitrate, hydrochloride, and sulphate; with phenylcarbimide, the oxamidine forms a *compound*, $C_{18}H_{20}O_4N_4$, which crystallises from alcohol in needles or prisms, melts at 183°, and has no basic properties. The oxamidine differs from Tiemann's amidoximes, $R{\cdot}C(NH_2){:}NOH$, in that it has no basic properties and is not stable towards alkalis, and is therefore regarded as the isomeride, $NH{:}CR{\cdot}NH{\cdot}OH$. T. M. L.

Dialkylamino-*o*-benzoylbenzoic Acids and their Derivatives. By ALBIN HALLER and ALFRED GUYOT (*Bull. Soc. Chim.*, 1901, [iii], **25**, 165—174).—Mainly a summary of work already published (Abstr., 1894, i, 602; 1898, i, 670). *Benzylethylaminobenzoylbenzoic acid*, $C_7H_7{\cdot}NEt{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H$, prepared by the condensation of benzylethylaniline with phthalic anhydride in presence of aluminium chloride, forms pale yellow needles and melts at 172°. N. L.

Dialkylaminobenzylbenzoic Acids derived from the Benzoyl Acids. II. By ALBIN HALLER and ALFRED GUYOT (*Bull. Soc. Chim.*, 1901, [iii], **25**, 200—205).—Most of the results contained in this paper have been previously published (Abstr., 1898, i, 670). Dimethylaminobenzylbenzoic acid melts at 173°.

Benzylethylaminobenzylbenzoic acid forms small, colourless crystals melting at 145°. The *methyl* ester is an uncrystallisable liquid which gives a red violet coloration with lead peroxide.

Dimethylamino-*m*-hydroxybenzylbenzoic acid melts at 204°.

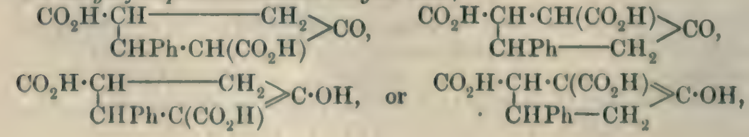
*Diethylamino-*m*-hydroxybenzylbenzoic acid* crystallises in colourless needles melting at 194°. N. L.

Addition of Diethyl Succinate to αβ-Unsaturated Ketones and Esters. By HANS STOBBE (*Annalen*, 1901, **315**, 219—246. Compare this vol., i, 147).—[With RICHARD FISCHER].—*β-Phenylbutane-αγδ-tricarboxylic* (*β-phenyl-*n*-butanetricarboxylic*) *acid*,

$$CO_2H{\cdot}CH_2{\cdot}CHPh{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H,$$

prepared from diethyl succinate and ethyl cinnamate, separates from dilute aqueous solutions in lustrous, triclinic crystals, which begin to soften at 181°, and melt, evolving gas, at 199—200°; the *calcium* and *barium* salts contain $2\frac{1}{2}H_2O$ and $5H_2O$ respectively, whilst the *silver* salt decomposes spontaneously even when protected from light. The *trimethyl* ester crystallises from petroleum in highly refractive prisms, and melts at 54—55°.

3-*Phenyl*cyclo*pentanonedicarboxylic acid*,

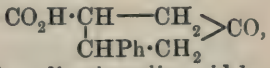


$$\begin{array}{l}CO_2H{\cdot}CH\text{———}CH_2\\ \quad\;|\\ \quad CHPh{\cdot}CH(CO_2H)\end{array}\!\!>CO,\qquad \begin{array}{l}CO_2H{\cdot}CH{\cdot}CH(CO_2H)\\ \quad\;|\\ \quad CHPh\text{——}CH_2\end{array}\!\!>CO,$$

$$\begin{array}{l}CO_2H{\cdot}CH\text{———}CH_2\\ \quad\;|\\ \quad CHPh{\cdot}C(CO_2H)\end{array}\!\!\geqslant C{\cdot}OH,\quad\text{or}\quad \begin{array}{l}CO_2H{\cdot}CH{\cdot}C(CO_2H)\\ \quad\;|\\ \quad CHPh\text{—}CH_2\end{array}\!\!\geqslant C{\cdot}OH,$$

the methyl ester of which is obtained by the action of sodium methoxide on the foregoing methyl ester, has not been isolated, because sodium hydroxide regenerates β-phenylbutane-αγδ-tricarboxylic acid; the *methyl* ester crystallises from petroleum or alcohol in white needles and melts at 94°. The *sodium* salt forms slender white needles, and the *copper* salt crystallises in pale green needles which contain 1 mol. of alcohol and melt at 145—147°; the *semicarbazone* crystallises from alcohol and melts at 162—163°.

3-*Phenyl*cyclo*pentanone-4-carboxylic acid*,



$$\left.\begin{array}{l}CO_2H\cdot CH\text{——}CH_2\\ \quad\;\, CHPh\cdot CH_2\end{array}\right>CO,$$

prepared from the methyl ester of the foregoing dicarboxylic acid by the action of hot 30 per cent. sulphuric acid, crystallises from hot water and melts at 117—118°; the *silver* salt is indifferent towards light, and the *semicarbazide* derivative, $C_{12}H_{12}ON_2$, which is not the normal semicarbazone, melts and decomposes at 208°. When 3-phenyl*cyclo*pentanone-4-carboxylic acid is oxidised with nitric acid, *α-phenyltricarballylic* (*α-phenylpropane-αβγ-tricarballylic*) *acid*,

$$CO_2H\cdot CHPh\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H,$$

is produced; it crystallises from water, and melts at 199°, when it decomposes vigorously. M. O. F.

Constitution of the Oxime Hydrochlorides. By Thor Ekecrantz (*Öfvers. Svenska Vetensk.-Akad. Förhandl.*, 1899, **56**, 985—1002).—The author has studied the relations between α- and β-*p*-nitrobenzaldoximes, their behaviour towards solvents, &c.

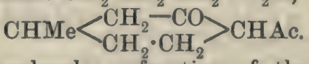
The α-oxime melts at 128·5—129° and separates from water in dark yellow, rhombic needles showing a deep blue colour when viewed parallel to the long direction of the crystals. The hydrochloride, when treated with sodium carbonate, yields the β-oxime, which separates from amyl alcohol in long, well-formed plates, showing strong double refraction and melting at 174—175°.

When determined in the ordinary way in capillary tubes, the melting points of the hydrochlorides of the α- and β-oximes are the same (about 112—117°), but when the salts are heated in test-tubes about 1·5 cm. wide, hydrogen chloride is copiously evolved, and fusion is not complete until a temperature of about 134° is reached, the two in this case also having the same melting point; on extracting the two tubes when cold, they are found to contain the α-oxime melting at 128·5—129°.

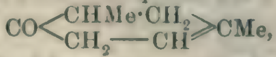
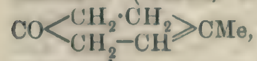
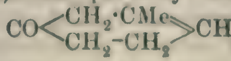
The action of various solvents on β-*p*-nitrobenzaldoxime was examined, and it was found that alcohol and ethyl acetate effect a partial transformation into the α-modification.

On methylating the hydrochlorides of the two oximes by means of diazomethane, the methyl ester of the α-oxime is obtained in both cases. T. H. P.

[Condensation of] Benzaldehyde with Propaldehyde. By Theodor Hackhofer (*Monatsh.*, 1901, **22**, 95—108).—In presence of a concentrated solution of potassium carbonate, benzaldehyde and propaldehyde condense to an *aldol*, OH·CHPh·CHMe·CHO, which breaks up into its components on all attempts at distillation. The *oxime*, $C_{10}H_{13}O_2N$, forms white crystals melting at 100°. On reduction of the aldol by aluminium amalgam, a *dihydric alcohol*, $C_{10}H_{14}O_2$, is obtained as a thick yellow liquid, which boils at 171° under 14 mm. and at 280° under atmospheric pressure; the *diacetate*, $C_{10}H_{12}O_2Ac_2$, distils at 180—185° under 13 mm., and at 287—290° under atmospheric pressure. By the action of a concentrated solution of sodium acetate on the aldol, water is eliminated and β-phenyl-α-methylacraldehyde is formed. When treated with sulphuric acid, the dihydric alcohol yields β-phenyl-α-methylpropaldehyde. K. J. P. O.

Cyclic β-Diketones. II. By Georges Leser (*Bull. Soc. Chim.*, 1901, [iii], **25**, 196—199. Compare Abstr., 1900, 1, 430).—The ketonic acid, $C_9H_{16}O_3$, obtained, as formerly described (*loc. cit.*), by the hydrolysis of acetylmethyl*cyclo*hexanone, yields β-methyladipic acid on oxidation with chromic acid, and has therefore the constitution $CH_2Ac\cdot CHMe\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2H$, whilst the hexanone has the constitution  $CHMe<\begin{matrix}CH_2-CO\\CH_2\cdot CH_2\end{matrix}>CHAc$. The latter formula is in accord with the molecular refraction of the compound (found, 43·9; calculated, 43·7).

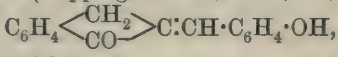
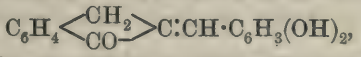
4-*Acetyl*-1:4-*dimethyl*-3-cyclo*hexanone*, prepared by treating acetylmethyl*cyclo*hexanone with sodium and methyl iodide, is a colourless liquid which boils at 114—116° under 11 mm. pressure, has a mol. refraction 46·28 (calculated 46·39), and forms a crystalline monoxime melting at 122—123°; it does not exhibit the characteristic reactions of β-diketones, since it gives no coloration with ferric chloride, does not form a copper salt, and is insoluble in alkalis. On treatment with dilute potash, it undergoes hydrolysis, partly into acetic acid and 1:4-*dimethyl*-3-cyclo*hexanone*, partly with the formation of *ζ-keto-βε-dimethyloctoic acid*. The last is an oily liquid which boils at 181—182° under 12 mm. pressure, and forms a crystalline *silver* salt. 1:4-Dimethyl-3-*cyclo*hexanone boils at 172—174° under 750 mm. pressure, and has a sp. gr. 0·9083 at 13°, $[\alpha]_D$ +11·6°, and a mol. refraction 37·13 (calculated 37·01). It forms an *oxime* crystallising in silky needles melting at 97—98°, and a semicarbazone melting at 176—177°. N. L.

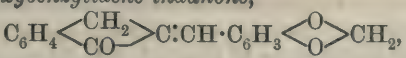
Ketones of Wood Oil. Dimethyl*cyclo*hexenone. By Auguste Béhal (*Compt. rend.*, 1901, **132**, 342—345).—One of the series of ketones extracted by the author from wood tar (Abstr., 1899, i, 121) has the composition $C_8H_{12}O$, boils at 194°, forms an oxime melting at 102·5° and a benzoyl derivative melting at 129°, and when oxidised with potassium permanganate yields acetic and α-methyllævulic acids. From these results, it is concluded that the ketone in question is a *dimethyl*cyclo*hexenone* of the constitution  $CO<\begin{matrix}CHMe\cdot CH_2\\CH_2-CH\end{matrix}>CMe$, and hence, judging by analogy, the methyl*cyclo*hexenone previously described (Abstr., 1898, i, 403) has probably the constitution  $CO<\begin{matrix}CH_2\cdot CH_2\\CH_2-CH\end{matrix}>CMe$, and not  $CO<\begin{matrix}CH_2\cdot CMe\\CH_2-CH_2\end{matrix}>CH$, as formerly suggested.

According to Bischoff, α-methyllævulic acid boils at 247—248°, but the author finds that when distilled, even under diminished pressure, it loses water and yields a *lactone* which boils at 205—206° and has a sp. gr. 1·0588 at 0°. N. L.

2-Hydroxybenzylacetophenone. By W. FEUERSTEIN and A. MUSCULUS (*Ber.*, 1901, **34**, 409—412).—The 2-hydroxybenzylacetophenone obtained by Kostanecki and Feuerstein (Abstr., 1898, i, 370) by the action of dilute acids on 2-hydroxybenzylidenediacetophenone, is converted by reduction with sodium amalgam into dihydrocoumaryl alcohol, $OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CHPh\cdot OH$ (Abstr., 1896, i, 302), and its constitution is thus proved.

2-*Methoxybenzylacetophenone*, $OMe\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot COPh$, is a viscid oil which boils at 223° under 20 mm. pressure. The o-*nitrophenylhydrazone* crystallises in orange-red needles melting at 120—121°. A. H.

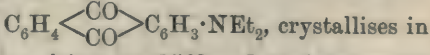
Some Substituted Benzylideneindanones. By W. FEUERSTEIN (*Ber.*, 1901, **34**, 412—415).—Indanone reacts with substituted aldehydes in the same manner as with benzaldehyde (Kipping, Trans., 1894, **65**, 428). o-*Hydroxybenzylideneindanone*,  $C_6H_4<\begin{smallmatrix}CH_2\\CO\end{smallmatrix}>C:CH\cdot C_6H_4\cdot OH$, crystallises in lustrous, yellow needles, which melt and decompose at 206°. m-*Hydroxybenzylideneindanone* crystallises in small, yellow prisms melting at 198—199°. p-*Hydroxybenzylideneindanone* crystallises in faintly yellow needles which melt at 219—220°. mp-*Dihydroxybenzylideneindanone*,  $C_6H_4<\begin{smallmatrix}CH_2\\CO\end{smallmatrix}>C:CH\cdot C_6H_3(OH)_2$, prepared from protocatechuic aldehyde, crystallises in deep yellow needles melting at 255—256°; as a dye, it produces orange-yellow shades with an alumina mordant. m-*Methoxy*-p-*hydroxybenzylideneindanone* was prepared from vanillin, and forms microscopic, yellow crystals melting at 187°. mp-*Methylenedioxybenzylidene indanone*,

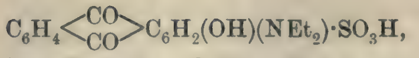


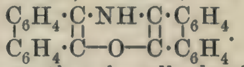
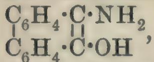
$$C_6H_4<\begin{smallmatrix}CH_2\\CO\end{smallmatrix}>C:CH\cdot C_6H_3<\begin{smallmatrix}O\\O\end{smallmatrix}>CH_2,$$

prepared from piperonal, crystallises in long, yellowish, lustrous needles and melts at 179—180°. p-*Dimethylaminobenzylideneindanone* forms golden, lustrous plates melting at 165—166°. A. H.

Preparation and Properties of Dialkylaminoanthraquinones. III. By ALBIN HALLER and ALFRED GUYOT (*Bull. Soc. Chim.*, 1901, [iii], **25**, 205—213. Compare Abstr., 1898, i, 593).—The dialkylaminobenzylbenzoic acids (this vol., i, 276) are readily converted by the action of concentrated sulphuric acid into dialkylaminoanthranols, which, when oxidised with ferric chloride, yield successively the corresponding oxanthranols and anthraquinones.

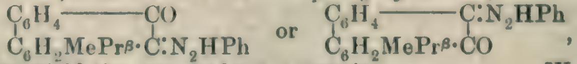
Diethylaminoanthraquinone,  $C_6H_4<\begin{smallmatrix}CO\\CO\end{smallmatrix}>C_6H_3\cdot NEt_2$, crystallises in red prisms, needles, or scales melting at 156°. *Benzylethylaminoanthraquinone* crystallises in large, red needles melting at 131°, and readily forms sulphonic derivatives, substitution probably occurring in the benzyl group. *Diethylaminohydroxyanthraquinonesulphonic acid*,

 $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_2(OH)(NEt_2)\cdot SO_3H$, from diethylamino-*m*-hydroxybenzylbenzoic acid, crystallises in slender, bronze-coloured needles; the *barium*, *calcium*, and *magnesium* salts crystallise well. *Diethylaminodihydroxyanthraquinone*, obtained by fusing the preceding compound with potash or soda at 200°, crystallises from toluene in large, violet-black needles, and from alcohol in red needles containing $1H_2O$. This compound does not dye with metallic mordants and is therefore concluded to be a quinizarin derivative, having the two hydroxyl groups in the meta-position with regard to each other. *Dimethylaminohydroxyanthraquinonesulphonic acid* is difficult to obtain in the pure state, and differs from the preceding compound in that it cannot be fused with potash without destruction of the NMe_2 group and in yielding a slaty black, crystalline precipitate with copper sulphate solution. N. L.

Action of Phenylhydrazine on Phenanthraquinone. By EUGEN BAMBERGER and JACOB GROB (*Ber.*, 1901, **34**, 533—539).—Phenylhydrazine reacts explosively with dry phenanthraquinone, but the action takes place quietly when ether is used as a solvent, nitrogen being evolved, and ammonia, benzene, and diphenyl formed, along with *phenanthroxazine*,  $\begin{array}{l}C_6H_4\cdot C\cdot NH\cdot C\cdot C_6H_4\\ C_6H_4\cdot C{-}O{-}C\cdot C_6H_4\end{array}$. The formation of the oxazine is probably due to the phenylhydrazine initially reducing the quinone to phenanthraquinol, the latter immediately combining with the ammonia produced to form the aminohydroxyphenanthrene,  $\begin{array}{l}C_6H_4\cdot C\cdot NH_2\\ C_6H_4\cdot C\cdot OH\end{array}$, 2 mols. of which condense to yield the oxazine, with elimination of $2H_2O$. Phenanthroxazine crystallises from boiling nitrobenzene or naphthalene in slender, bronze-coloured needles with a metallic lustre, melts at 350—355° (uncorr.), and sublimes at a higher temperature in reddish-brown scales; it is indifferent to acids and alkalis, and is not changed when boiled for several hours with acetic anhydride. In presence of zinc chloride, however, the anhydride gives rise after a few minutes to an *acetyl* derivative, which crystallises from amyl alcohol in slender, yellowish-white needles, and melts somewhat indefinitely at about 330°.

The constitution of phenanthroxazine follows from its yielding phenanthrazine when treated with gaseous ammonia in nitrobenzene solution at 130—140°; that it is formed from phenanthraquinone as just explained is shown by its production along with phenanthrazine when gaseous ammonia is passed into phenanthraquinol dissolved in cumene at 120—130°.

Retenequinone interacts with phenylhydrazine in ethereal solution to form ammonia, benzene and the *monophenylhydrazone*,



$$\begin{array}{l}C_6H_4\text{———}CO\\ C_6H_2MePr^{\beta}\cdot C{:}N_2HPh\end{array}\quad\text{or}\quad\begin{array}{l}C_6H_4\text{———}C{:}N_2HPh\\ C_6H_2MePr^{\beta}\cdot CO\end{array},$$

but fails to yield the expected reteneoxazine. W. A. D.

New Preparation of Terpineol. By P. GENVRESSE (*Compt. rend.*, 1901, 132, 637—639. Compare Abstr., 1900, i, 351).—When a mixture of pinene, alcohol, and nitrous acid (purified from nitric acid) is left at the ordinary temperature, reaction slowly takes place, and at the end of two months about two-thirds of the pinene is transformed. By fractional distillation of the product, first with steam and then alone under reduced pressure, a liquid is obtained which is identical in its chemical and physical properties with terpineol; the yield is about 75 per cent. of the pinene transformed. The melting point of the nitrosochloride, which seems not to have been recorded, was found to be 83°. Australene, when similarly treated, yields *d*-terpineol. Limonene gave a negative result. N. L.

New Alcohol derived from Limonene. By P. Genvresse (*Compt. rend.*, 1901, **132**, 414—416. Compare Abstr., 1900, i, 351).—*Limonenol*, $C_{10}H_{16}O$, produced by the action of nitrous fumes on *d*-limonene cooled by ice and salt, is separated from the crude product, after neutralisation with sodium carbonate, by distillation in steam, and finally separated from unaltered hydrocarbon by extraction with a concentrated solution of sodium salicylate, this solvent having the property of dissolving terpenoid alcohols, but not terpenes. The compound is a colourless liquid having an agreeable odour, differing from that of pinenol or limonene; it boils without decomposition at 135° under 15 mm. pressure and has $[\alpha]_D + 19°21'$ at 17°, a sp. gr. 0·9669 at 18°, and n_D 1·497. Its molecular refraction deduced from experimental data is 45·99, which corresponds with the value 46·5 calculated from Brühl's constants, on the assumption that the compound contains two double linkings. This assumption is justified by the fact that the alcohol absorbs 2 mols. of bromine without the evolution of hydrogen bromide.

Limonenone, $C_{10}H_{14}O$, a colourless liquid having an agreeable odour, is prepared by oxidising the preceding compound with chromic acid mixture; at 20°, it has $[\alpha]_D + 16°4'$, n_D 1·487, and a sp. gr. 0·9606 at 20°. The molecular refraction calculated from the refractive index is 44·858, and from Brühl's constants 45·16, assuming two double linkings.

Limonenoxime, $C_{10}H_{14}\text{:}NOH$, produced by treating the preceding ketone with alcoholic solutions of hydroxylamine hydrochloride and potassium hydroxide, is purified by distillation in steam; it melts at 85·5°, but if, after allowing the fused mass to solidify, the melting point is redetermined, it is found to have fallen to 72°. Small quantities of the oxime result from the action of nitrous fumes on limonene. The compound seems to be identical with *l*-carvoxime, the melting point of the latter corresponding with the lower melting point of the former; the substances have the same $[\alpha]_D$, namely, $-39°42'$, whilst the benzoyl and phenylcarbimide derivatives agree in properties melting at 95° and 133° respectively. G. T. M.

Observations on Oximes and their Reduction to the corresponding Amines. By Michael I. Konowaloff (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 45—48).—Contrary to the statement generally made, that camphoroxime has in solution a molecular weight twice as great as that required by its formula, the author finds that in freezing benzene the molecular weight varies from 202·1 to 279·7 for concentrations between the limits 3 and 0·07 per cent.

Nägeli (Abstr., 1883, 728) stated that camphoroxime is completely stable towards concentrated hydrochloric acid at 100—120°. The author finds, however, that when heated with hydrochloric acid in a sealed tube for an hour at 120°, camphoroxime yields campholenic acid.

According to Leuckart and Bach (Abstr., 1887, 376), camphoroxime gives only small quantities of bornylamine when reduced with sodium in alcoholic solution. By gradually adding sodium to a solution of the oxime in alcohol, the author obtains a yield equal to 55 per cent. of the theoretical of bornylamine, with properties almost identical with those of the amine described by Leuckart and Bach.

By the reduction of diphenylnitromethane by tin and hydrochloric acid, and by the reduction of an alcoholic solution of benzophenoneoxime by means of sodium, identical specimens of benzhydrylamine were obtained with the boiling point 301—302° under 746 mm. pressure, this temperature being 288—289°, according to Leuckart and Bach (Abstr., 1886, 1023), and Michaelis and Linow (*Ber.*, 1893, **26**, 2168). The sp. gr. of benzhydrylamine is 1·0635 at 21·5°/0°, and n_D 1·59631 at 21·5°, giving for the molecular refraction according to the Lorentz and Lorenz formula the value 58·57. Benzhydrylamine *nitrate*, melting at about 200°, *oxalate* melting at about 185—188°, and *aurichloride* melting at 152—154° are described. T. H. P.

Fenchene and Camphene. By IWAN L. KONDAKOFF and EUGEN LUTSCHININ (*Chem. Zeit.*, 1901, **25**, 131—133. Compare Abstr., 1900, i, 604).—The authors have isolated one of the two constituents of fenchene in a pure form. It boils at 140—141°, has a sp. gr. 0·8385 at 20°/20° $[\alpha]_D$ −55°, and shows the properties of a reduced aromatic compound with a double linking in the ring. The isomeride probably has a double linking attached to a tertiary carbon atom in the side chain.

Fenchyl iodide, $C_{10}H_{17}I$, obtained by the action of a solution of hydrogen iodide saturated at −20° on fenchyl alcohol at the ordinary temperature, boils at 120—123° under 23 mm. pressure, has a sp. gr. 1·4199 at 21°/4°, and a slight lævorotation. On treatment with alcoholic potash, it yields a fenchene boiling at 148—158°, and having a sp. gr. 0·8519 at 22°/22° and $[\alpha]_D$ +2°4′ at 40°. Fenchene hydriodide, $C_{10}H_{17}I$, obtained from this hydrocarbon distils at 120—120·5° under 23 mm. pressure, has a sp. gr. 1·427 at 21°/4° and $[\alpha]_D$ +42°57′ at 40°; when treated with alcoholic potash, it gives a fenchene boiling at 143—150°, and of sp. gr. 0·8482 at 19°/4°, together with some unaltered hydriodide; the latter reacts with moist silver oxide, yielding solid fenchyl alcohol.

Camphene hydriodide, which should be identical with *iso*bornyl iodide, forms colourless crystals melting at 48—55°, and when treated with alcoholic potash gives a camphene melting at 49°, and having $[\alpha]_D$ −5°55′, together with unaltered iodide. This iodide reacts with silver oxide, yielding camphene and probably borneol (compare Wagner, Abstr., 1900, i, 96, 554). J. J. S.

Eucalyptus Oil containing 60 per cent. of Geranyl Acetate. By HENRY G. SMITH (*Chem. News*, 1901, **83**, 5).—Fresh leaves and branchlets of *Eucalyptus Macarthuri* collected in October and distilled with steam yielded 0·112 per cent. of oil. The oil has a sp. gr. 0·9245 at 15°, a rotation of $+3{\cdot}6°$ in a 100 mm. tube, is soluble in 70 per cent. alcohol, and contains 60 per cent of geranyl acetate, 10·64 per cent. of free alcohol calculated as geraniol, as well as eudesmol, which crystallised from the fraction distilling between 266° and 282°.

D. A. L.

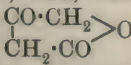
Empyreaumatic Oil of Juniper. By CATHELINEAU and JEAN HAUSSER (*Bull. Soc. Chim.*, 1901, [iii], **25**, 247—250. Compare Abstr., 1899, i, 536, 711, and 1900, i, 510).—The results of the fractional distillation of that portion of empyreaumatic oil of juniper which is insoluble in sodium hydroxide have already been given (Abstr., 1899, i, 536). The investigation of the chemical nature of the various fractions thus obtained is, however, unsatisfactory, neither have processes based on steam distillation and extraction led to the separation of any well characterised individual substances. N. L.

New Case of Chloroform of Crystallisation: Leprarin-Chloroform. By GEORG KASSNER (*Arch. Pharm.*, 1901, **239**, 44—48).—Leprarin (Zopf, Abstr., 1897, i, 437), of which the correct composition is $C_{19}H_{18}O_9$, crystallises from chloroform with $1CHCl_3$. Other cases of chloroform of crystallisation are cited. C. F. B.

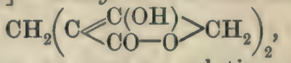
Polycystin, a Crystalline Carotin from Polycystis flos aquæ. By WILHELM ZOPF (*Chem. Centr.*, 1901, i, 466; from *Ber. bot. Ges.*, **18**, 461—467).—Polycystin, a crystalline carotin, has been isolated from the alcoholic extract of *Polycystis flos aquæ.* It separates from its solution in ether as a red, crystalline mass formed of long, slender needles and broad, rhombic leaflets, and has a metallic lustre. Its solutions are not fluorescent. The spectra of the light petroleum, ether, alcohol, and chloroform solutions are described in the original paper; they do not show the chlorophyll spectrum, and are not identical with that of the carotin from the carrot or from solanorubin. Polycystin is a eucarotin, for it does not combine with alkalis or with alkaline earths. E. W. W.

Bilifuscin. By LEO R. VON ZUMBUSCH (*Zeit. physiol. Chem.*, 1901, **31**, 446—459).—Bilifuscin has been isolated from human biliary calculi in the form of an almost black powder having the composition $C_{64}H_{96}O_{14}N_7$. It shows no trace of crystalline structure, dissolves sparingly in chloroform, methyl alcohol, amyl alcohol, or acetone, but fairly readily in acetic acid, naphthalene or dimethylaniline, and also in alkalis.

The nitrogen cannot be estimated by any of the ordinary modified Kjeldahl processes, and although numerous experiments have been made, it has not been settled in what form the nitrogen is evolved when bilifuscin is heated with fuming sulphuric acid. The pigment must certainly be very differently constituted from bilirubin. J. J. S.

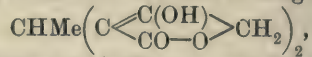
Condensation Products of Tetronic Acid. By LUDWIG WOLFF (*Annalen*, 1901, **315**, 145—173. Compare Abstr., 1900, i, 582).—Tetronic acid,  $\left.\begin{array}{l}CO\cdot CH_2\\ \,| \\ CH_2\cdot CO\end{array}\right>O$, undergoes condensation with aldehydes, ketones, and ketonic acids, surpassing acetoacetic and malonic esters in activity. The action has been studied in respect of formaldehyde, acetaldehyde, benzaldehyde, acetone, acetophenone, pyruvic acid, and diacetyl, and takes place without the assistance of a condensing agent; anhydrotetronic acid (Abstr., 1896, i, 524) also undergoes condensation with aldehydes, but *a*-substituted tetronic acids are indifferent.

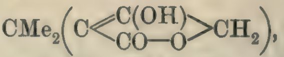
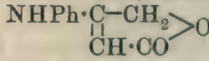
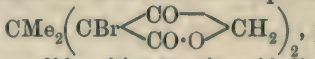
[With W. Schimpff].—*Methylenebistetronic acid*,



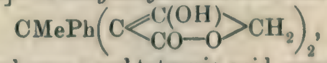
$$\mathrm{CH_2}\left(\mathrm{C}<\begin{matrix}\mathrm{C(OH)}\\ \mathrm{CO-O}\end{matrix}>\mathrm{CH_2}\right)_2,$$

precipitated on mixing an aqueous solution of tetronic acid with formaldehyde, crystallises from a mixture of alcohol and petroleum in plates which melt and evolve gas at 245°; the *calcium* salt contains $3H_2O$, and the *barium* salt crystallises from water in long needles.

Ethylidenebistetronic acid,  $\mathrm{CHMe}\left(\mathrm{C}<\begin{matrix}\mathrm{C(OH)}\\ \mathrm{CO-O}\end{matrix}>\mathrm{CH_2}\right)_2$, crystallises from hot water in lustrous prisms, and after recrystallisation from a mixture of alcohol and petroleum melts at 209—210°, evolving gas; it is identical with the bye-product obtained on preparing tetronic acid from bromotetronic acid and a reducing agent (Abstr., 1896, i, 523). Like the foregoing substance, ethylidenebistetronic acid develops a red coloration with ferric chloride; hot aniline converts it into anilinotetronic acid, and sodium nitrite gives rise to oximinotetronic acid.

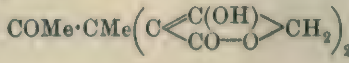
iso*Propylidenebistetronic acid*,  $\mathrm{CMe_2}\left(\mathrm{C}<\begin{matrix}\mathrm{C(OH)}\\ \mathrm{CO-O}\end{matrix}>\mathrm{CH_2}\right)$, crystallises in needles, and melts, decomposing, at 200—201°; it requires 50—60 parts of boiling alcohol to dissolve it, and on continued heating with the solvent is resolved into tetronic acid and the acid $C_{14}H_{16}O_6$ melting at 120°. The *dibenzoyl* derivative crystallises from alcohol in lustrous leaflets and melts at 162°. Phenylhydrazine converts *iso*propylidenebistetronic acid into the phenylhydrazide of tetronic acid, whilst aniline gives rise to the *anilide* of tetronic acid,  $\begin{matrix}\mathrm{NHPh\cdot C-CH_2}\\ \| \\ \mathrm{CH\cdot CO}\end{matrix}>\mathrm{O}$, which crystallises from alcohol in silky needles and melts at 220°. When *iso*propylidenebistetronic acid is heated with an aqueous solution of hydroxylamine hydrochloride, the *compound* $C_{11}H_{13}O_6N$ is produced, separating from alcohol in well-formed crystals which melt at 158° and immediately resolidify; the substance cannot be regarded as the normal oxime, because it does not develop colour with ferric chloride. The *dibromide*,  $\mathrm{CMe_2}\left(\mathrm{CBr}<\begin{matrix}\mathrm{CO-}\\ \mathrm{CO\cdot O}\end{matrix}>\mathrm{CH_2}\right)_2$, prepared by the action of bromine on *iso*propylidenebistetronic acid dissolved in moist chloroform, crystallises from a mixture of petroleum and dry chloroform in lustrous prisms, and melts at 113°, when it decomposes; it is neutral towards sodium carbonate, and is slowly decomposed by hot water, yielding bromotetronic and bistetronic acids.

[With M. Gabler].—*Phenylethylidenebistetronic acid*,



$$\mathrm{CMePh}\left(\mathrm{C}<\begin{matrix}\mathrm{C(OH)}\\ \mathrm{CO-O}\end{matrix}>\mathrm{CH_2}\right)_2,$$

prepared from acetophenone and tetronic acid, crystallises from alcohol and melts, evolving gas, at 169—171°.

Ketobutylidenebistetronic acid,  $\mathrm{COMe\cdot CMe}\left(\mathrm{C}<\begin{matrix}\mathrm{C(OH)}\\ \mathrm{CO-O}\end{matrix}>\mathrm{CH_2}\right)_2$,

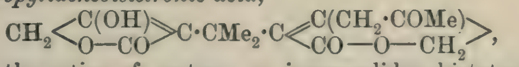
obtained from diacetyl and tetronic acid, crystallises from a mixture of benzene and methyl alcohol, and melts somewhat indefinitely at 144°, when it decomposes; the oxime crystallises in lustrous plates, which become yellow at 175° and decompose at about 208°.

Propiobistetronic acid, $CO_2H\cdot CMe\left(C<\genfrac{}{}{0pt}{}{C(OH)}{CO—O}>CH_2\right)_2$, derived from tetronic and pyruvic acids, crystallises in large, lustrous prisms containing $1H_2O$, and melts at 196°, when it decomposes.

The *compound*, $C_{18}H_{14}O_{10}$, produced on adding acetaldehyde to a cold concentrated aqueous solution of anhydrotetronic acid, crystallises in needles containing $3H_2O$, and melts at 120°; the anhydrous compound melts and decomposes at 247°.

Tetronic acid undergoes condensation with mesityl oxide, yielding the *acid*, $C_{14}H_{16}O_6$, which crystallises from dilute alcohol in lustrous needles and melts, evolving gas, at 230°; *ketohexyltetronic acid*, $COMe\cdot CH_2\cdot CMe_2<\genfrac{}{}{0pt}{}{C(OH)}{CO—O}>CH_2$, accompanies it, and crystallises from hot water in lustrous pyramids, which sinter at 120° and melt at 122—124°.

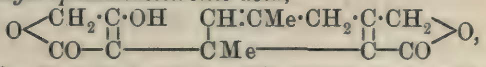
Acetonylpropylidenebistetronic acid,



$$CH_2<\genfrac{}{}{0pt}{}{C(OH)}{O—CO}>C\cdot CMe_2\cdot C<\genfrac{}{}{0pt}{}{C(CH_2\cdot COMe)}{CO—O—CH_2}>,$$

prepared by the action of acetone on *iso*propylidenebistetronic acid in alcoholic, aqueous, or hydrochloric acid solution, crystallises from dilute alcohol in aggregates of small needles containing $1H_2O$, which is removed at 80°; when dried in air, the substance sinters at 115°, melts, evolving gas at 120°, then resolidifies, and finally fuses at 162—163°, but after dehydration in a vacuum or at 80°, it becomes yellow at about 130°, and melts at 165—167°. The *benzoyl* derivative crystallises from alcohol in large, lustrous prisms, and melts at 134—135°; the *oxime* separates in four-sided, colourless plates, and melts, evolving gas, at 180°. The oxime reduces silver nitrate and Fehling's solutions, and is resolved by glacial acetic acid into tetronic acid, a nitrogenous compound which decomposes at 212°, and a *base*, $C_{10}H_{11}O_2N$, which crystallises from hot alcohol in lustrous, white needles, and melts at 151—152°.

Dimethyldihydrophthalidetetronic acid,



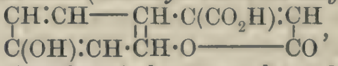
$$O<\genfrac{}{}{0pt}{}{CH_2\cdot C\cdot OH \qquad CH{:}CMe\cdot CH_2\cdot C\cdot CH_2}{CO—C———CMe———C—CO}>O,$$

prepared by heating acetonylpropylidenebistetronic acid with barium carbonate suspended in water, crystallises from alcohol in yellow plates or lustrous prisms, and melts at 250°, evolving gas; bromine converts it into the *compound*, $C_{14}H_{11}O_5Br$, which crystallises from a mixture of chloroform and petroleum in colourless prisms melting and decomposing at 178°. M. O. F.

Coumarins from Phenol. By HANS VON PECHMANN and E. VON KRAFFT (*Ber.*, 1901, **34**, 421—423).—4-Methylcoumarin is best prepared by treating a mixture of ethyl acetoacetate and phenol with cold concentrated sulphuric acid; the yield is never more than 3 per cent. The melting point of the pure product is 81—82° (not 125—126°, Pechmann and Duisberg, Abstr., 1884, 66). *Ethyl coumarin-4-carboxylate*, obtained by the condensation of phenol and ethyl oxalacetate by means of concentrated sulphuric acid, crystallises in slender, colourless needles melting at 77—78°, and when hydrolysed with alcoholic potash yields the corresponding *acid*, which crystallises in small needles and melts at 179—180°. R. H. P.

Coumarins from 1 : 2 : 4-Trihydroxybenzene. By HANS VON PECHMANN and E. VON KRAFFT (*Ber.*, 1901, **34**, 423—426).—1 : 2 : 4-Trihydroxybenzene, when condensed with ethyl acetoacetate by means of concentrated sulphuric acid or an alcoholic solution of zinc chloride, yields 4-*methylæsculetin*, which crystallises in small, yellowish, lustrous needles and melts at 269—270°. *Ethyl æsculetin-4-carboxylate*, formed from ethyl oxalacetate with 1 : 2 : 4-trihydroxybenzene, crystallises in yellow needles with $\frac{1}{2}H_2O$, melts at 207—208° and, when hydrolysed, yields the corresponding *acid*, which crystallises with H_2O and melts at 295°. Ethyl æsculetin-4-carboxylate, when treated successively with potash and methyl iodide, forms the *dimethyl ether* of æsculetin-4-carboxylic acid; this crystallises in golden needles, melts at 241—244°, and forms a *silver* salt, which, when distilled with steam, yields æsculetin dimethyl ether. *Ethyl æsculetin-3-carboxylate*, obtained by the condensation of 2 : 3 : 5-trihydroxybenzaldehyde with ethyl malonate, crystallises in lustrous brown tablets, melts at 244—245°, and when hydrolysed yields the corresponding *acid*, crystallising in small, yellow needles and melting and decomposing at 270°. R. H. P.

7-Hydroxycoumarin-4-carboxylic Acid. By HANS VON PECHMANN and ERDMANN GRAEGER (*Ber.*, 1901, **34**, 378—386).—7-*Hydroxycoumarone-4-carboxylic acid* (*umbelliferone-4-carboxylic acid*),



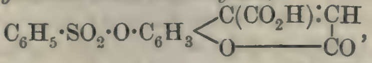
$$\begin{matrix} CH{:}CH\text{—}CH{\cdot}C(CO_2H){:}CH \\ C(OH){:}CH{\cdot}CH{\cdot}O\text{———}CO \end{matrix},$$

prepared by hydrolysing the ethyl ester, melts at 247—248°, separates from water in minute needles containing $1\frac{1}{2}H_2O$, or in forms containing $2H_2O$, and in alkaline solution shows a yellow colour and gradually develops a green fluorescence. The *ethyl* ester, $C_{12}H_{10}O_5$, prepared by the action of sodium ethoxide on an alcoholic solution of ethyl oxaloacetate and resorcinol, crystallises from hot water or alcohol in yellow prisms with a greenish reflection, melts at 153—154°, and dissolves in alkalis; a red bye-product is described which becomes yellow at about 300°, and sublimes without melting. The *methyl* ester, prepared by condensing in methyl alcoholic solution, is less soluble than the ethyl ester, crystallises from dilute alcohol in greenish-yellow prisms, and melts at 178°.

7-*Methoxycoumarone-4-carboxylic acid*, $C_{11}H_8O_5$, prepared by hydrolysing its methyl ester, crystallises from hot water or alcohol in yellow needles, melts at 219°, and is converted into 7-methoxycoumarone by the dry distillation of the silver salt. The *methyl* ester, $C_{12}H_{10}O_5$, separates from wood-spirit as a yellow, crystalline powder and melts at 115°.

7-*Acetoxycoumarone-4-carboxylic acid*, $C_{12}H_8O_6$, crystallises from hot water in felted, silky needles, melts at 193°, and is converted by heat into 7-acetoxycoumarone; the *ethyl* ester, $C_{14}H_{12}O_6$, crystallises from dilute alcohol in white, felted needles and melts at 118—119°. *Ethyl 7-benzoyloxycoumarone-4-carboxylate*, $C_{19}H_{14}O_6$, crystallises from dilute alcohol in white needles and melts at 118°.

Methyl-7-p-bromobenzoyloxycoumarone-4-carboxylate, $C_{18}H_{11}O_6Br$, crystallises from dilute alcohol in white needles and melts at 98°. *Methyl-7-benzenesulphonoxycoumarone-4-carboxylate*,

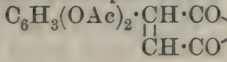


$$C_6H_5\cdot SO_2\cdot O\cdot C_6H_3<\begin{matrix}C(CO_2H):CH\\ |\\ O\text{———————}CO\end{matrix},$$

crystallises from benzene in white prisms and melts at 171·5°.

β-2 : 4-Dihydroxyphenylmaleic (resorcylmaleic) acid,

$$C_6H_3(OH)_2\cdot C(CO_2H):CH\cdot CO_2H,$$

prepared by the action of baryta on 7-hydroxycoumaronecarboxylic acid, melts and decomposes at 187—188°. *β-2 : 4-Diacetoxyphenylmaleic anhydride*,  $C_6H_3(OAc)_2\cdot\begin{matrix}CH\cdot CO\\ \|\\ CH\cdot CO\end{matrix}>O$, crystallises in white needles and melts at 121—122°.

8-Bromo-7-hydroxycoumarone-4-carboxylic acid, $C_{10}H_5O_5Br$, crystallises from dilute alcohol in yellow needles and melts at 260°. The *ethyl* ester crystallises from alcohol or acetone in golden-yellow, felted needles and melts at 203°.

7-Hydroxycoumarone-3-carboxylic acid, $C_{10}H_6O_5$, separates from dilute alcohol as a colourless, crystalline powder, loses water at 105°, and melts at 262°, and, unlike the isomeride described above, is readily decomposed by heat into carbon dioxide and umbelliferone. The *ethyl* ester, $C_{12}H_{10}O_5$, prepared from resorcinaldehyde, malonic acid, and piperidine, crystallises from dilute alcohol in white, glistening needles or flakes, loses water at 100°, and melts at 165—170°. T. M. L.

Solubilities of Alkaloids in Carbon Tetrachloride. By IWAN SCHINDELMEISER (*Chem. Zeit.*, 1901, **25**, 129).—The following numbers give the weights of alkaloids soluble in 100 parts of pure carbon tetrachloride at 17°. Morphine, 0·032; codeine, 1·328; papaverine, 0·203; narceine, 0·011; atropine, 1·136; cocaine, 18·503; strychnine, 0·645; brucine, 1·973. The alkaloids used were in all cases crystalline, and were previously finely ground and dried for 2 weeks over quicklime. J. J. S.

Hydrocinchonine. By ÉMILE JUNGFLEISCH and EUGÈNE LÉGER (*Compt. rend.*, 1901, **132**, 410—412. Compare *ibid.*, 1869, **69**, 284).—The authors now find that the base cinchonifine extracted by them from crude cinchonine by the action of dilute sulphuric acid is not isomeric but identical with hydrocinchonine obtained by oxidising the alkaloid with potassium permanganate. The two preparations have when pure, the same melting point, 278° (corr.), and specific rotation 198·6—199·5°; their double zinc chlorides are chemically and crystallographically identical. There is still some discrepancy between the sulphates, that obtained from hydrocinchonine by Skraup and also by Först and Bœhringer is said to contain $12H_2O$, whilst the authors' preparation from cinchonifine crystallises with $2H_2O$ from concentrated, and with $11H_2O$ from dilute solutions; the hydrated salts containing 11 and $12H_2O$ appear, however, to be similar in crystalline form, solubility (1 in $30H_2O$), and melting point, 195°; they are, moreover, both optically active in the solid state. G. T. M.

Corybulbine. By JOHANNES GADAMER and D. BRUNS (*Arch. Pharm.*, 1901, **239**, 39—44. Compare Dobbie, Lauder, and Paliatseas, Trans., 1901, **79**, 87).—Corybulbine has $[\alpha]_D$ +303·3° at 20° in chloroform solution. Dehydrocorybulbine hydriodide was obtained crystallised with $1H_2O$, not 2 (Ziegenbein, Abstr., 1897, i, 175); the base is reduced by zinc and sulphuric acid to i-*corybulbine*, which is optically inactive, and melted (it was perhaps impure) at 220°.

C. F. B.

Cytisine. By MARTIN FREUND and ADOLF FRIEDMANN (*Ber.*, 1901, **34**, 605—619).—Cytisine interacts with aqueous hydrogen peroxide at the ordinary temperature as a secondary base, the imino-group being converted into the *iso*nitroso-group, $N\cdot OH$ (compare Mamlock and Wolffenstein, Abstr., 1900, i, 209). The product of the action, *hydroxycytisine*, $C_{11}H_{13}NO\colon N\cdot OH$, crystallises from water or alcohol, melts and decomposes at 223—226°, is not changed by boiling concentrated mineral acids or alkalis, and readily reduces warm ammoniacal silver nitrate or Fehling's solution; no definite product could be obtained by its oxidation with alkaline potassium permanganate, or on heating with methyl iodide at 100°. It is indifferent to phenylthiocarbimide, and does not liberate iodine from either neutral or acid solutions of potassium iodide. The *hydrochloride*,

$$C_{11}H_{14}O_2N_2,2HCl,\tfrac{1}{2}H_2O,$$

forms rhombic octahedra and melts and decomposes at 270°, whilst the *platinichloride* does not melt at 325°; the *nitrate*, with $1H_2O$, melts at 145—147°, the anhydrous salt melting at 100°. The *acetyl* derivative, $C_{11}H_{13}NO\colon N\cdot OAc$, crystallises from water or alcoholic ether and melts at 117°. With aqueous sulphurous acid, hydroxycytisine yields the *sulphamic acid*, $C_{11}H_{13}NO\colon N\cdot SO_3H,2H_2O$, which crystallises from water in stellate aggregates of needles, decomposes at 280°, and when boiled with hydrochloric acid is hydrolysed quantitatively to sulphuric acid and cytisine.

As stated by Partheil (Abstr., 1891, **231**, 750) cytisine is converted by warm concentrated nitric acid into a *nitronitrosocytisine*, and the same substance is formed on slowly adding nitrosocytisine (von Buchka and Magalhaẽs, Abstr., 1891, 750) to well-cooled fuming nitric acid; when heated with alcoholic hydrogen chloride at 100°, it loses the nitroso-group and yields *nitrocytisine hydrochloride*,

$$NO_2\cdot C_{11}H_{13}ON_2,HCl,$$

which crystallises from its concentrated aqueous solution, and decomposes at 270—280°. *Nitrocytisine*, $C_{11}H_{13}O_3N_3$, crystallises from absolute alcohol in beautiful, yellow, rhombic prisms, melts at 185—188°, and combines with phenylthiocarbimide to form the *thiocarbamide*, $C_{18}H_{18}O_3N_4S$, which crystallises from nitrobenzene in yellow leaflets and melts and decomposes at 252—253°.

Acetylnitrocytisine, $NO_2C_{11}H_{12}NO\colon NAc$, obtained either by the action of acetic anhydride on the nitro-base, or, in small yield only and in an impure state, by warming acetylcytisine with concentrated nitric acid of sp. gr. 1·4, crystallises from alcohol in lance-like needles and melts at 223—225°. *Aminocytisine,* formed on reducing nitrocytisine with tin and hydrochloric acid, is a viscous oil; the *hydrochloride,* $C_{11}H_{15}ON_3,2HCl$, crystallises from water on adding alcohol in stout, four-sided prisms, and melts at 305°. All attempts to convert aminocytisine into a hydroxycytisine through the diazo-reaction failed, ill-defined products only being formed.

Acetylaminocytisine, $NH_2 \cdot C_{11}H_{12}NO:NAc$, obtained by carefully reducing nitroacetylcytisine in the cold with tin and hydrochloric acid, separates from chloroform on adding light petroleum, melts at 242—245°, and when boiled with hydrochloric acid yields aminocytisine hydrochloride; like aminocytisine, it yields no definite product on diazotisation.

As stated by Lammers (*Arch. Pharm.*, 1897, **235**, 374), hydriodic acid at 180—190° does not act on cytisine; after heating for 4 hours at 225°, however, in presence of amorphous phosphorus, complete decomposition occurs, ammonia being formed along with a small quantity of a *base,* $C_{11}H_{14}ON_2$, which crystallises from alcohol in beautiful needles, softens at 182°, and melts at 187°; its salts are decomposed by water, but it can be heated with concentrated sulphuric acid or aqueous potassium hydroxide without change.

Cytisine condenses with aqueous formaldehyde at the ordinary temperature to form *methylenedicytisine,* $CH_2(C_{11}H_{13}ON_2)_2$, which crystallises best from toluene and melts at 212°. W. A. D.

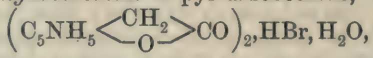
Damascenine, a Constituent of the Seeds of Nigella Damascena. By HERBERT POMMEREHNE (*Arch. Pharm.*, 1901, **239**, 34—39).—A further account is given of the *isomeride* of damascenine, formed when the latter substance is heated with alcoholic potash (Abstr., 1900, i, 684). It has the composition $C_9H_{11}O_3N,3H_2O$, melts at 76—77°, or at 140—141° when anhydrous, and has an acid as well as a basic character, neutralising 1NaOH. As stated already, the salts which it forms with acids are practically identical with those of damascenine itself. C. F. B.

Compounds of Bismuth Chloride with Organic Bases. By LUDWIG VANINO and OTTO HAUSER (*Ber.*, 1901, **34**, 416—420).—A solution of bismuth chloride in acetone is precipitated by aromatic bases. Many of these, however, such as aniline, methyl-, and dimethylaniline, and *o*- and *p*-toluidine do not yield simple compounds, whilst others yield definite crystalline derivatives.

Quinoline bismuth chloride, $C_9H_7N,BiCl_3$, is a white, crystalline mass, which is only slowly decomposed by water and is not hygroscopic. If free hydrochloric acid be present, the salt, $(C_9H_7N,HCl)_2,BiCl_3$, is also formed. *Quinoline bismuth iodide,* C_9H_7N,BiI_3, is formed as a red crystalline powder when quinoline bismuth chloride is added to boiling aqueous potassium iodide. *Quinoline hydrochloride bismuth chloride,* $C_9H_7N,HCl,BiCl_3$, is prepared by dissolving quinoline bismuth chloride in hydrochloric acid and evaporating. Pyridine bismuth chloride, $(C_5H_5N)_3(BiCl_3)_2$, has already been described by Montemartini (this vol., i, 163). *Pyridine bismuth iodide* is a deep red powder, which is soluble both in alcohol and aqueous potassium iodide, and decomposes when heated without melting.

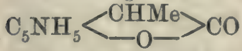
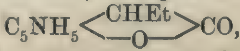
Pyridine hydrochloride bismuth chloride, $(C_5H_5N,HCl)_3(BiCl_3)_2$, is produced when pyridine bismuth chloride is dissolved in hydrochloric acid, and crystallises in very soluble needles. α-*Naphthylamine bismuth chloride*, $(C_{10}H_7{\cdot}NH_2)_2(BiCl_3)_3$, is a voluminous crystalline precipitate which is readily decomposed by water. α-*Naphthylamine bismuth iodide*, $(C_{10}H_7{\cdot}NH_2)_2BiI_3$, crystallises in long, fascicular groups of deep red needles, and is decomposed by water. Bismuth chloride in acetone solution also gives precipitates with anhydroformaldehydeaniline and with cocaine. A. H.

Action of Monohaloid Aliphatic Acids on Pyridine and Quinoline. By L. J. Simon and L. Dubreuil (*Compt. rend.*, 1901, **132**, 418—421. Compare Krüger, Abstr., 1890, 1431; 1891, 941, 1388).—The *basic hydrobromide* of pyridinebetaine,



$$\left(C_5NH_5<\!\begin{smallmatrix}CH_2\\O\end{smallmatrix}\!>CO\right)_2,HBr,H_2O,$$

produced by mixing monobromoacetic acid (2 mols.) and pyridine (3 mols.) in alcoholic solutions, separates in white crystals; quinoline behaves similarly, yielding the *hydrobromide*, $(C_{11}H_9NO)_2,HBr,H_2O$. The corresponding hydrochlorides of pyridine and quinoline betaines are formed in a similar manner and also crystallise with $1H_2O$.

This reaction has been extended to other monohaloid acids of the acetic series, and it is found that the action becomes less vigorous as the homologous series is ascended; the *hydrobromides* of the betaines,  $C_5NH_5<\!\begin{smallmatrix}CHMe\\O\end{smallmatrix}\!>CO$ and  $C_5NH_5<\!\begin{smallmatrix}CHEt\\O\end{smallmatrix}\!>CO$, have been obtained in this investigation.

When monobromosuccinic acid acts on the tertiary amine, the reaction takes a different course, hydrogen bromide is eliminated, and the salt of the corresponding unsaturated acid is formed; in the case of quinoline, a well-defined crystalline *quinoline fumarate* has been isolated. G. T. M.

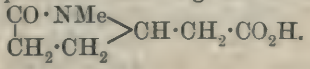
Nitrostilbazoles. By Karl Feist (*Ber.*, 1901, **34**, 464—467. Compare Baurath, Abstr., 1888, 65 and 608; Roth, this vol., i, 165).—Nitrostilbazoles, $C_5NH_4{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NO_2$, are formed when molecular quantities of 2-picoline and *o*-, *m*-, or *p*-nitrobenzaldehyde are heated for 6 hours at 220—225°, either with or without the addition of zinc chloride. The products are best isolated in the form of their sparingly soluble mercuric chlorides.

o-*Nitrostilbazole* crystallises from dilute alcohol in colourless needles melting at 95—96°; the *hydrochloride* melts and decomposes at 206—212°; the *aurichloride* is a sparingly soluble greyish-yellow amorphous precipitate, as is also the *platinichloride*, which melts and decomposes at 220—224°; the *dibromide*, $C_{13}H_{10}O_2N_2Br_2$, crystallises in colourless prisms melting at 167—168°.

m-*Nitrostilbazole* crystallises in yellowish plates melting at 127°; the *hydrochloride* forms glistening, yellow needles which slowly decompose at 200°; the *aurichloride* melts at 187°; the *platinichloride* melts and decomposes at 240°; and the *dibromide* forms prismatic needles melting at 153°.

p-*Nitrostilbazole* melts at 125—126° and readily turns red on exposure to the air. The *hydrochloride* does not crystallise readily, and melts at 140—180°; the *mercurichloride*, $(C_{13}H_{10}O_2N_2,HCl)_2HgCl_2,H_2O$, crystallises in sparingly soluble, reddish-yellow needles melting at 195°; the *aurichloride* melts and decomposes at 205°; the *platinichloride* at 206—207°; and the *dibromide* forms pale-yellow crystals melting at 173°. J. J. S.

Ecgonic Acid. By RICHARD WILLSTÄTTER and ADOLF BODE (*Ber.*, 1901, **34**, 519—523).—*d*-Ecgonic acid obtained along with *d*-tropic acid by oxidising tropine with chromic acid in sulphuric acid solution, crystallises from ethyl acetate or benzene in colourless needles, melts at 93—95° (compare Liebermann, Abstr., 1891, 749), and contains one methyl group attached to nitrogen. *l*-Ecgonic acid obtained similarly from *l*-ecgonine has the properties assigned to it by Liebermann, and also contains one methyl group; the *methyl* ester, $C_8H_{13}O_3N$, is colourless, boils at 275° under 13·5 mm. pressure, and does not react with phenylhydrazine or hydroxylamine. It does not yield a nitrosoamine or a benzoyl derivative, and is not changed by methyl iodide at the ordinary temperature. These facts are not in accord with Liebermann's formula for the acid, even when correction is made for recent views as to the true nature of tropine and ecgonine (Abstr., 1898, i, 178). It is probable that ecgonic acid is a 1-*methylpyrrolidone-2-acetic acid*,



$$\left.\begin{matrix}CO\cdot NMe\\ |\\ CH_2\cdot CH_2\end{matrix}\right>CH\cdot CH_2\cdot CO_2H.$$

W. A. D.

Nitroformaldehyde Phenylhydrazone. By EUGEN BAMBERGER and OTTO SCHMIDT (*Ber.*, 1901, **34**, 574—594. Compare Abstr., 1894, i, 183; 1900, i, 566).—Nitroformaldehyde phenylhydrazone, $NO_2\cdot CH⁚N_2HPh$, exists in two, presumably stereoisomeric, modifications. The *a*-compound crystallises from benzene, light petroleum, or chloroform and forms long, orange-red, glistening, monoclinic prisms melting at 74·5—75·5°. The *β*-isomeride crystallises from alcohol in small, golden-yellow needles melting at 84·5—85·5°, and is less readily soluble in most organic solvents. Either compound, when warmed with different solvents, is partially converted into its isomeride. Both phenylhydrazones react as pseudo-acids, and give rise to *sodium* salts, which are to be regarded as derived from the *iso*nitro-compounds; they form orange-yellow, flat needles with a bronzy lustre. So far it has not been settled whether the two sodium derivatives are identical or not; when acted on by hydrochloric acid, they are immediately transformed into the normal nitro-compounds.

Nitroformazyl is obtained when the *a*-phenylhydrazone is kept for some three years, or when it is treated with potassium *iso*diazobenzene, or when either the *a*- or *β*-compound reacts with phenyldiazonium chloride or with almost any acid. Phenylformazyl (Abstr., 1894, i, 183) is produced when an alkaline solution of normal diazobenzene acts on the *a*-phenylhydrazone.

A *methyl ether*, $OMe\cdot NO⁚CH\cdot N⁚NHPh$, produced when either the *a*- or *β*-phenylhydrazone reacts with diazomethane in ethereal solution, forms dark, orange-red, glistening needles melting at 54·5°, and readily soluble in organic solvents. When kept for several days it decomposes, yielding a brown syrup; very dilute sulphuric acid converts it into formaldehyde and a compound, $NPh{:}N{\cdot}CH{:}N{\cdot}OH$.

A N-*methyl ether*, $NMePh{\cdot}N{:}CH{\cdot}NO_2$, obtained by methylating the *a*- or *β*-sodium salt, crystallises from light petroleum in pale yellow, hair-like needles melting at 91—92°, and readily soluble in organic solvents but insoluble in alkalis; when reduced with zinc dust and acetic acid, it yields *as*-phenylmethylhydrazine, but when reduced with stannous chloride it also yields monomethylaniline and *phenylmethylhydrazidine*, $NO_2{\cdot}CH{:}N{\cdot}NMePh$, which crystallises in flat needles melting at 101°; with nitrous acid it gives a greenish-blue changing to blue coloration, and with ferric chloride, a pale green. The same ester may be obtained by the action of dibromonitromethane on *as*-phenylmethylhydrazine; other products formed at the same time are the *bromohydrazo*-compound, $NMePh{\cdot}NH{\cdot}CHBr{\cdot}NO_2$, melting at 98—100°, and pale yellow plates melting at 216—218°. J. J. S.

Acetylamidrazone. By Eugen Bamberger and Jacob Grob (*Ber.*, 1901, **34**, 539—548).—The following facts show that acetylamidrazone (Bamberger and Lorenzen, Abstr., 1893, i, 157; Bamberger and de Gruyter, Abstr., 1894, i, 98; Jagerspacher, Abstr., 1895, i, 573) has the structure $NH_2{\cdot}CAc{:}N{\cdot}NHPh$. With benzaldehyde, it yields the *benzylidene* derivative, $CHPh{:}N{\cdot}CAc{:}N{\cdot}NHPh$, which crystallises from alcohol in strongly refracting, orange-red prisms, softens at 156° and melts at 159—159·5° (corr.). Formaldehyde gives rise to the analogous *methylene* derivative, $CH_2{:}N{\cdot}CAc{:}N{\cdot}NHPh$, which crystallises from light petroleum in orange needles, melts at 136—136·5°, and is apparently decomposed when crystallised from alcohol or acetone, the product melting at 180—190°. Nitrous acid at 0° converts acetylamidrazone into ammonia (1 mol.), and the tautomeric form, $OH{\cdot}CAc{:}N{\cdot}NPh{\cdot}NO$, of *nitrosopyruvic acid phenylhydrazide*; this in aqueous-alcoholic solution reddens litmus, and dissolves readily in alkalis, including sodium carbonate and ammonia. It crystallises from ether in stellate aggregates of transparent prisms, softens at 78°, melts and decomposes at 85—85·5°, and slowly decomposes in the air; it is very sensitive to oxidising agents. It yields a *phenylhydrazone*, $N_2HPh{:}CMe{\cdot}C(OH){:}N{\cdot}NPh{\cdot}NO$, which crystallises from chloroform on adding light petroleum in nearly white, silky needles, melting and decomposing at 128—129° in a bath previously heated to 110—115°. The p-*nitrophenylhydrazone* is much more stable, and crystallises from boiling alcohol in beautiful, golden leaflets, which melt and decompose at 147—148°. When the hydrazide is warmed with hydrochloric acid, it yields the phenylhydrazone, $N_2HPh{:}CMe{\cdot}CO_2H$, of pyruvic acid, owing probably to the isomeric change of the compound,

$$N_2HPh{:}CAc{\cdot}OH,$$

initially formed; diazobenzene chloride, phenol, aniline, nitrosobenzene and, probably, diazobenzeneimide are formed as bye-products.

W. A. D.

Acid and Alcoholic Compounds of Phenylcarbazide or Phenylhydrazine Ureide. By Paul Cazeneuve (*Compt. rend.*, 1901, **132**, 340—342).—Molecular *compounds* of phenylcarbazide with formic, acetic, propionic, *n*-butyric, valeric, and oxalic acids are obtained by dissolving the carbazide in the acid or in a solution thereof, and cooling the solution obtained. They are crystalline substances which decompose when boiled with water, or when heated a little below 100°. Phenylcarbazide crystallises from its solutions in methyl, ethyl, *iso*propyl, amyl, or benzyl alcohols with 1 mol. of the alcohol; these *compounds* are decomposed by water, and are less stable than the acid compounds. Phenylcarbazide also combines with phenols and with aldehydes. N. L.

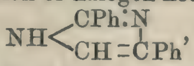
Preparation of *as*-Secondary Benzalhydrazines from Benzaldazines. By THEODOR CURTIUS and H. FRANZEN (*Ber.*, 1901, **34**, 552—559. Compare Abstr., 1900, i, 610).—2 : 4 : 5-Trimethylbenzaldazine may be reduced to the corresponding dibenzylamine by mixing it with zinc dust, and adding this in small portions to boiling alcohol alternately with a solution of glacial acetic acid in alcohol. *Di*-2 : 4 : 5-*trimethylbenzylamine*, $NH(CH_2\cdot C_6H_2Me_3)_2$, crystallises in snow-white needles melting at 78°. The *sulphate* crystallises in small, white needles melting at 189°, the *hydrochloride* melts at 226° and the *nitrate* melts and decomposes at 203—204°. The *platinichloride* forms brownish-yellow plates. The *nitrite*, $NH(CH_2\cdot C_6H_2Me_3)_2,HNO_2$, crystallises in white needles which melt and decompose at 148°. When boiled for some time with alcohol, it yields the *nitrosoamine*, $NO\cdot N(CH_2\cdot C_6H_2Me_3)_2$, which crystallises in spherical aggregates of faintly yellow-coloured needles melting at 85°. On reduction with zinc dust and acetic acid in presence of alcohol at 10—15°, it yields *di*-2 : 4 : 5-*trimethylbenzylhydrazine*, $NH_2\cdot N(CH_2\cdot C_6H_2Me_3)_2$, the *hydrochloride* of which crystallises in snow-white needles melting at about 203°. *Benzylidenedi*-2 : 4 : 5-*trimethylbenzylhydrazine*, $CHPh\colon N\cdot N(CH_2\cdot C_6H_2Me_3)_2$, forms matted, white needles melting at 119°.

Benzaldazine can readily be reduced by the method just described, yielding dibenzylamine, the *nitrite* of which crystallises in white plates and melts at 130°. Boiling alcohol converts it slowly into dibenzylnitrosoamine, which is reduced by zinc dust and acetic acid in presence of alcohol at the ordinary temperature, yielding *as*-dibenzylhydrazine, which has previously been prepared by Busch and Weiss (Abstr., 1900, i, 699), who were, however, unable to obtain it in this way. Dibenzylhydrazine is converted by oxidation with mercuric oxide in presence of chloroform into *dibenzyltetrazone*,

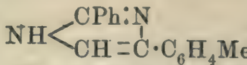
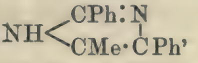
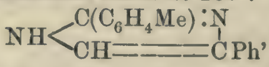
$$N(CH_2Ph)_2\cdot N\colon N\cdot N(CH_2Ph)_2,$$

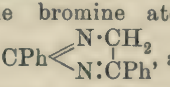
which crystallises in needles melting at 97°. A. H.

Preparation of Substituted Iminazoles [Glyoxalines]. By FRANZ KUNCKELL (*Ber.*, 1901, **34**, 637—642).—Substituted iminazoles can be prepared by the action of halogen-ketones on the amidines.

2 : 4-*Diphenylglyoxaline*,  $NH{<}\begin{matrix}CPh\colon N\\ \quad\;|\\ CH{=}CPh\end{matrix}$, prepared by the action of bromoacetophenone on benzamidine, crystallises from alcohol in small, white needles, and melts at 193°. The *hydrochloride*, $C_{15}H_{13}N_2Cl$, dissolves in hot water and alcohol and melts at 264°. The *silver* salt, $C_{15}H_{11}N_2Ag$, forms a white, flocculent precipitate. Methyl and ethyl iodides, and bromoacetophenone form additive compounds with the

glyoxaline, which are converted into unstable ammonium bases by the action of alkalis or silver oxide, and then pass into 1-methyl, 1-ethyl, or 1-phenacyl-glyoxalines.

2-*Phenyl*-4-p-*tolylglyoxaline*,  $NH<\begin{matrix}CPh:N\\ CH=C\cdot C_6H_4Me\end{matrix}$, crystallises from benzene and melts at 183°. The isomeric 2 : 4-*diphenyl*-5-*methylglyoxaline*,  $NH<\begin{matrix}CPh:N\\ CMe\cdot CPh\end{matrix}$, prepared by the action of α-bromopropiophenone on benzamidine, melts at 215°; the *hydrochloride* crystallises from alcohol in white needles and melts at 280°. The third isomeride, 4-*phenyl*-2-*tolylglyoxaline*,  $NH<\begin{matrix}C(C_6H_4Me):N\\ CH=\!=\!=CPh\end{matrix}$, is produced by the action of *p*-tolenylamidine on bromoacetophenone, but is not described.

By the action of α-bromo*iso*butyrophenone on benzamidine, *benzamidino*iso*butyrophenone*, $NH:CPh\cdot NH\cdot CMe_2Bz$, is produced; it crystallises from dilute alcohol and melts at 175°; the *phenylhydrazone*, $C_{23}H_{24}N_4$, crystallises from alcohol in yellow needles and melts at 110°. The fact that a glyoxaline is not formed in this case indicates that the condensation does not take place between the bromine atom and the imino-hydrogen to form (for example)  $CPh<\begin{matrix}N\cdot CH_2\\ N:CPh\end{matrix}$, as this should also take place with the dimethyl derivative; the formation of a silver salt also indicates that the product contains an imino-group.

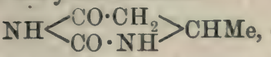
Phenacylidenebenzamidine, $NH:CPh\cdot N:CHBz$, prepared by the action of dibromoacetophenone on benzamidine, crystallises from alcohol in white needles and melts at 224°. T. M. L.

Derivatives of 1-Phenyl-2 : 3-dimethyl-5-pyrazolone (Antipyrine). By GUSTAV EBERT and BAPTIST REUTER (*Chem. Zeit.*, 1901, **25**, 43—44).—When aqueous solutions of phenyldimethylpyrazolonetrimethylammonium hydroxide, $C_3N_2Me_2PhO\cdot NMe_3\cdot OH$, are evaporated on the water-bath, or under reduced pressure, or are boiled with potassium hydroxide, the products formed are *acetyl*-s-*phenylmethylhydrazine* melting at 94° and betaine. *Diacetyl*-s-*phenylmethylhydrazine*, prepared by the action of acetic acid or anhydride on the monoacetyl compound, melts at 76—77°, but so far has not been converted into phenyldimethylpyrazolone.

The following salts of antipyrine have been prepared: the *acetylsalicylate* melting at 64—65°, *hydrogen camphorate* at 98—100°, and the *normal camphorate* at 95—98°.

4-*Dimethylamino*-1-*phenyl*-2 : 3-*dimethyl*-5-*pyrazolone salicylate* melts at 69—70°, the *acetylsalicylate* at 66—70°, the *normal camphorate* at 81—82°, and the *hydrogen camphorate* at 94°. J. J. S.

Synthesis of Thymine and Other Uracils. By EMIL FISCHER and GEORG ROEDER (*Sitzungsber. Akad. Wiss. Berlin*, 1901, **12**, 268—276).—Hydrouracils may be produced either by the interaction of potassium cyanate and the salts of the esters of β-amino-acids, or by heating carbamide with an unsaturated acid; the second mode of synthesis is preferable, since it obviates the necessity of preparing the amino-acid, and moreover the yield is better.

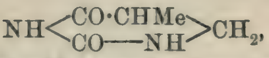
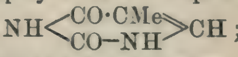
4-*Methyldihydrouracil*,  $NH<\begin{matrix}CO\cdot CH_2\\CO\cdot NH\end{matrix}>CHMe$, obtained by the two new synthetical methods, and also by heating β-aminobutyric acid with carbamide, crystallises from water or alcohol in lustrous plates, and melts at 219—220° (corr.); the yield from crotonic acid and carbamide is about 20 per cent. of the theoretical.

Ethyl β-aminobutyrate, prepared by esterifying a mixture of the corresponding acid with ethyl alcohol in the presence of hydrogen chloride, is a colourless liquid with an ammoniacal odour; it boils at 59—60° under 12 mm. pressure, and mixes in all proportions with water, alcohol, ether, or light petroleum. When treated with potassium cyanate and dilute sulphuric acid, it yields the preceding compound.

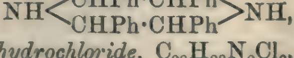
The *benzoyl* derivative and *phenylcarbimide* of β-aminobutyric acid crystallise from hot water in needles, and melt respectively at 155° and 148°; the latter substance, when heated with concentrated hydrochloric acid, yields a *compound* melting at 200°, which is probably a phenylmethyldihydrouracil.

Bromo-4-methyldihydrouracil, which contains the bromine atom either in position 4 or 5, is produced by heating 4-methyldihydrouracil at 100° with bromine and glacial acetic acid; it crystallises from alcohol in colourless needles and melts at 315—320°.

Methyluracil results from the action of a cold 15 per cent. solution of sodium hydroxide on the preceding compound; it melts at 320° and is identical with the product obtained by Gabriel from ethyl acetoacetate.

5-*Methyldihydrouracil* (*hydrothymine*),  $NH<\begin{matrix}CO\cdot CHMe\\CO—NH\end{matrix}>CH_2$, obtained from carbamide and methylacrylic acid, separates from water or alcohol in small crystals melting at 264—265° (corr.). This substance yields a bromo-derivative, which was employed in an impure state in the synthesis of thymine (5-methyluracil),  $NH<\begin{matrix}CO\cdot CMe\\CO—NH\end{matrix}>CH$; the latter compound, when thus prepared, is identical with the natural product isolated from the thymus of the calf by Kossel and Neumann. Thymine sinters at 318° and melts at 321°. Dihydrouracil, produced from acrylic acid and carbamide, melts at 275° and crystallises in four-sided plates. This description tallies with that of Tafel's, and it was not found possible to obtain the compound in the form of needles as indicated by Weidel and Roithner (Abstr., 1896, i, 470).

G. T. M.

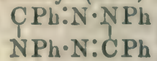
Synthesis of αβγδ-Tetraphenylpiperazine. By Julius Schmidt (*Ber.*, 1901, **34**, 627—629).—By reducing *s*-α- or β-diphenyldinitroethylene or *s*-diphenyldinitroethane with zinc dust and acetic acid, the hydrochloride of 2 : 3 : 5 : 6-*tetraphenylpiperazine*,  $NH<\begin{matrix}CHPh\cdot CHPh\\CHPh\cdot CHPh\end{matrix}>NH$, is produced; the *base* is a yellow oil; the *hydrochloride*, $C_{28}H_{28}N_2Cl_2$, crystallises from hot, strong hydrochloric acid in long, white needles, becomes brown at 249°, and melts at 254—256°; the *platinichloride*,

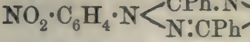
$C_{28}H_{26}N_2,H_2PtCl_6$, crystallises in golden-yellow, glistening flakes, and melts and decomposes vigorously at about 204°; the aurichloride is not well characterised; the *picrate* crystallises in yellow needles and melts at 185—187°. T. M. L.

Absorption of Light by Indophenols. By PIERRE BAYRAC and CHARLES CAMICHEL (*Compt. rend.*, 1901, **132**, 338—340. Compare Abstr., 1896, ii, 345, and this vol., i, 100).—The displacement of the absorption band in the red in the spectrum of indophenols containing a primary, instead of a tertiary, nitrogen atom in the para-position with regard to the nitrogen atom connecting the two nuclei may possibly occur, but is considered as not proved by the observations of Lemoult (this vol., i, 232). The authors find it impossible to define accurately the position of the extremities, and hence of the centre, of the band in the red. N. L.

Absorption Spectra of the Indophenols and of Dyes derived from Triphenylmethane. By CHARLES CAMICHEL and PIERRE BAYRAC (*Compt. rend.*, 1901, **132**, 485—487).—The indophenols of thymol, *o*-cresol, and phenol, derived from *p*-diaminobenzene, and therefore containing primary nitrogen, are much less opaque in alcoholic solution than the corresponding compounds containing tertiary nitrogen, but like the latter show a broad absorption band with one edge in the red and the other in the infra-red, and do not agree with Lemoult's law of auxochromes (this vol., i, 232).

Among the dyes derived from triphenylmethane, malachite-green, methyl-green, and crystal violet show absorption bands with one edge only in the visible red, and in these cases also the law of auxochromes does not hold good. The substitution of primary nitrogen for tertiary nitrogen, and the number of tertiary nitrogen atoms in the molecule, are important factors in determining the action of the substance on light, but the true laws have still to be discovered. With alcoholic solutions of the indophenols and aqueous solutions of triphenylmethane derivatives, the coefficient of absorption is proportional to the concentration of the solution. C. H. B.

Action of Sodium Methoxide on Phenylnitroformaldehydephenylhydrazone, and the Oxidation of Benzaldehydephenylhydrazone. By EUGEN BAMBERGER and JACOB GROB (*Ber.*, 1901, **34**, 523—532. Compare Abstr., 1899, i, 108).—Sodium methoxide reacts with phenylnitroformaldehydephenylhydrazone in methyl alcoholic solution to form benzoic acid and its methyl ester (about 30 per cent. of the total product), traces of benzanilide, and of a crystalline *base* melting at 109°, 1·5 per cent. of phenylformazyl (*Ber.*, 1894, **27**, 158), and 39 per cent. of *tetraphenyltetrazoline*,  $\begin{array}{l}\text{CPh:N}\cdot\text{NPh} \\ |\qquad\quad\;\; | \\ \text{NPh}\cdot\text{N:CPh}\end{array}$; the latter crystallises from a mixture of benzene and alcohol in long, amber-yellow or golden, lustrous needles, melts at 203—204°, and when distilled with zinc dust yields benzonitrile and aniline. Its constitution follows from its being formed by the oxidation of dehydrophenylbenzylidenehydrazine (Minunni and Rap, Abstr., 1897, i, 40) with sodium ethoxide and iodine, and as one of the products (about 8 per cent.)

obtained on subjecting benzaldehydephenylhydrazone to the same treatment (compare Ingle and Mann, Trans., 1895, **67**, 606; von Pechmann, Abstr., 1893, i, 461). On nitration in warm glacial acetic acid solution, it yields a *dinitro*-derivative, *β-dinitrotetraphenyltetrazoline*, which crystallises from xylene in short, lustrous, brownish-red needles, and melts when rapidly heated at 310°, and when slowly heated at 299° (uncorr.). An isomeric compound, *a-dinitrotetraphenyltetrazoline*,  $NO_2\cdot C_6H_4\cdot N\left<\begin{matrix}CPh\colon N\\ N\colon CPh\end{matrix}\right>N\cdot C_6H_4\cdot NO_2$, is formed when phenylnitroformaldehyde-*p*-nitrophenylhydrazone, $NO_2\cdot CPh\colon N_2H\cdot C_6H_4\cdot NO_2$, reacts with sodium methoxide in methyl alcoholic solution; it crystallises from xylene in slender, red needles and does not melt at 300°.

W. A. D.

Diphenylcarbodiazide. By Paul Cazeneuve (*Compt. rend.*, 1901, **132**, 412—414. Compare Abstr., 1900, i, 465).—Diphenylcarbodiazide is conveniently prepared by slowly adding a hot alcoholic solution of diphenylcarbazide (1 mol.) to a boiling aqueous solution of silver acetate (4 mols.), filtering off the precipitated silver, evaporating the filtrate to dryness, extracting the residue with methyl alcohol, and precipitating the colourless crystalline product by means of ether. The compound is soluble in hot water or the alcohols, and crystallises in lustrous, acicular lamellæ; it does not melt but decomposes violently at temperatures below 100°. Unlike its generator, diphenylcarbodiazide, it does not react with copper and mercury salts; when boiled with alcoholic alkali hydroxides, the solution assumes an orange tint owing to the formation of the alkali derivative of diphenylcarbazone. The acids of the acetic series dissolve diphenylcarbodiazide, and the solutions rapidly become solid owing to the formation of molecular compounds. These substances resemble diphenylcarbodiazide in their properties and are dissociated by heat; the formic acid compound may be considered to have the formula $NPh\colon N\cdot CO\cdot N\colon NHPh\cdot O\cdot CHO$.

The *dibromide*, $NPh\colon N\cdot CO\cdot NBr\cdot NBrPh$, produced by the direct addition of bromine, separates from alcohol in pale yellow crystals darkening at 60°; when boiled with alcoholic potassium hydroxide, it yields diphenylcarbazone and potassium bromide. G. T. M.

Compounds of Proteids with Aldehydes. By Leo Schwarz (*Zeit. physiol. Chem.*, 1901, **31**, 460—478. Compare Benedicenti, *Arch. physiol.*, 1897, 219).—Crystallised serum-albumin combines with formaldehyde, yielding a substance which is no longer coagulated on heating; it is precipitated from its solution by ammonium sulphate even when only partially saturated. The precipitate is not so readily soluble as the original albumin, and is not thrown down from its solutions by the aid of 96 per cent., or even of absolute, alcohol. When precipitated by a mixture of alcohol and ether, it is at first soluble in water, but after some time becomes insoluble. The behaviour of the product towards various reagents has been studied. Analyses have also been made, but these show that the composition varies with the length of time during which the formaldehyde is allowed to remain in contact with the albumin.

Acetaldehyde, propaldehyde, and to a certain extent heptaldehyde, behave similarly, but *iso*butaldehyde and *iso*valeraldehyde do not interfere with the coagulation of albumin. Benzaldehyde and salicylaldehyde give emulsions with serum-albumin solutions and no coagulation occurs on warming.

When a salt, for example, ammonium sulphate, is present, the aldehydo-compounds are much more readily precipitated.

Formaldehyde reacts in a similar manner with egg-albumin, serum-globulin, edestin, and heteroalbumose, but not with the iododerivative of egg-albumin.

In all cases, the number of aldehyde molecules added varies considerably with the length of time and probably with the aldehyde or proteid substance employed.

The aldehydo-compounds appear to be completely indifferent towards trypsin, and are only very slowly digested by pepsin.

J. J. S.

Gluco-proteid of Bone. By P. B. Hawk and William J. Gies (*Proc. Amer. Physiol. Soc.*, 1900, xv—xvi).—In its reactions, the mucin of bone (osseo-mucoid) is the same as Mörner's chondro-mucoid from cartilage. The average analysis of what are regarded as the purest of the seven specimens prepared comes out much the same as that given by Mörner; there is, however, rather more hydrogen and oxygen in the osseo-mucoid. W. D. H.

Iodohæmoglobin. By D. Kuraéeff (*Zeit. physiol. Chem.*, 1901, **31**, 527—542. Compare Abstr., 1898, i, 609; 1899, i, 314).—Oxyhæmoglobin has been converted into an iodo-derivative by the action of a solution of iodine in potassium iodide either in the presence of sodium hydrogen carbonate or of potassium iodate; when the latter method is employed, the product appears to be more readily soluble in alkali. *Iodohæmoglobin* (11·02—12·5 per cent. of iodine) forms a dark coloured precipitate which dries to a solid mass with a glistening, black fracture and when ground forms a brownish-black powder. The crude product is almost insoluble in alcohol or dilute acids, and its alkaline solutions give no precipitate with calcium hydroxide, but with barium hydroxide a substance is deposited which appears to have all the properties of iodohæmoglobin. After purification by the aid of sodium hydroxide, it dissolves in all alkalis, and even in dilute (0·5 per cent.) hydrochloric acid; the acid solution gives an absorption spectrum which appears to be identical with that given by an acid solution of hæmatin or of methæmoglobin. Experiments have been made on the action of pepsin salts and of trypsin on iodohæmoglobin.

Crystallised hæmin gives rises to an *iodo*-derivative containing 14·31 per cent. of iodine; it is readily soluble in alkalis or in alcohol containing a few drops of sulphuric acid, and is not so readily precipitated as iodohæmoglobin by ammonium sulphate from its alkaline solutions.

J. J. S.

Constitution of the Hæmatic Acids. By William Küster (*Annalen*, 1901, **315**, 174—218. Compare this vol., i, 58).—The imide of tribasic hæmatic acid, $C_8H_9O_4N$, obtained by oxidising hæmatin with chromic acid, crystallises from hot water in aggregates of colourless needles, and from ether in monoclinic, holohedral crystals [$a : b : c = 0·5808 : 1 : 0·7138$;

$\beta = 87°44·0'$]; it is very readily soluble in water, alcohol, ether, or chloroform, melts at 113·5—114·5°, is optically inactive, and has the electrical conductivity K 0·00366 at 25°. The *ammonium* salt melts at 100° and decomposes at 170°, the *calcium* salt contains $1H_2O$, the *zinc* salt separates from ether in monoclinic, holohedral crystals, and the *cadmium*, *mercury*, *silver*, and *hydrogen silver* salts are also crystalline.

The conversion of the foregoing imide into the anhydride of tribasic hæmatic acid is effected, not only by sodium hydroxide, but also under the influence of sodium carbonate, magnesium hydroxide, ammonium hydroxide, 50 per cent. sulphuric acid, and hydrogen bromide at 130°. The anhydride melts at 96—97°, and crystallises from ether in the rhombic system [$a : b : c = 0·533 : 1 : ?$]. It dissolves with some difficulty in chloroform or benzene, but readily in alcohol, ether, or glacial acetic acid; it is optically inactive, and has the electrical conductivity K 0·0229. The *potassium*, *ammonium*, *strontium*, *barium*, and *silver* salts have been analysed.

The remaining portions of the paper have been already noticed (*loc. cit.*), and the introductory part contains an exhaustive summary of previous work.
M. O. F.

Nucleohiston. By Ivar Bang (*Zeit. physiol. Chem.*, 1901, **31**, 407—410). By Albrecht Kossel (*ibid.*, 410).—A continuation of the controversy between these authors (compare this vol., i, 57).
J. J. S.

Guanylic Acid. By Ivar Bang (*Zeit. physiol. Chem.*, 1901, **31**, 411—427. Compare Abstr., 1899, i, 179).—When guanylic acid is hydrolysed by the aid of mineral acids, it yields guanine, glycerol, a pentose, and phosphoric acid according to the equation $C_{44}H_{66}O_{34}N_{20}P_4 + 10H_2O = 4C_5H_5ON_5 + 3C_5H_{10}O_5 + 3C_3H_8O_3 + 4H_3PO_4$. This composition for the acid is supported by analyses of it and of its silver salt, and a constitutional formula is also proposed; the glycerol is probably contained in the form of glycerophosphoric acid, and guanylic acid is thus related to the lecithins, but bears no close relationship to inosinic acid as Kossel suggests.
J. J. S.

Nucleic Acids. By Albrecht Kossel (*Zeit. physiol. Chem.*, 1901, **31**, 428—431).—A polemical reply to Bang (compare preceding abstract).
J. J. S.

Composition of Nucleic Acids. By P. A. Levene (*Proc. Amer. Physiol. Soc.*, 1900, viii—ix. Compare Abstr., 1900, i, 572).—Two varieties of paranucleic acid gave very similar results on analysis:

	C.	H.	N.	P.
From vitellin	32·31	5·58	13·13	9·88
From ichthulin	32·56	6·00	14·00	10·34

Nucleic acids from different sources gave more divergent results:

	C.	N.	N.	P_2O_5
From pancreas	36·50	4·69	16·70	20·16
„ codfish sperm ...	36·73	5·12	16·78	20·47
„ tubercle bacilli	33·78	6·32	9·42	29·40

The acid obtained from pancreas contains adenine in addition to guanylic acid. In the preparation of nucleic acid, glycogen is precipitated simultaneously. The two can be separated by copper chloride; the copper salt of nucleic acid is insoluble, that of glycogen soluble in water. W. D. H.

Paranucleic Acid. By P. A. Levene and C. Alsberg (*Zeit. physiol. Chem.*, 1901, **31**, 543—555. Compare Abstr., 1900, ii, 555).—Vitellin is the name given by the authors to the paranucleo-compounds in yolk of egg, and the acid which may be obtained from this is called *avivitellic acid.* The *copper* salt has been prepared and analysed; it contains 12·36 per cent. of copper; the composition varies, however, slightly in different specimens. The acid is insoluble in water, alcohol, ether, or dilute acids, but dissolves in solutions of acetates, especially ammonium acetate. The salts of the alkalis are soluble, but those of the alkaline earths insoluble, in water. The sodium and potassium salts become insoluble in water when left in contact with alcohol. All specimens of the acid give Millon's reaction, but this may be due to an impurity. When hydrolysed with hydrochloric acid, it gives melanin, arginine, histidine, and probably lysine. The proteid part of the molecule is not a protamine, but the acid is probably an ester of albumin with phosphoric acid. J. J. S.

Aromatic Chlorophosphines and their Derivatives. By August Michaelis (*Annalen*, 1901, **315**, 43—103. Compare Abstr., 1897, i, 48).—[With Paul Güsewell].—*Diphenylmethanechlorophosphine*, $CH_2Ph\cdot C_6H_4\cdot PCl_2$, prepared from diphenylmethane, phosphorus trichloride, and aluminium chloride, is a colourless, viscous liquid which boils at 221° under 20 mm. pressure, and has a sp. gr. 1·182 at 17°; the *tetrachloride* melts at 80°, and the *oxychloride*, $C_{13}H_{11}\cdot POCl_2$, boils at 261° under 20 mm. pressure, and has a sp. gr. 1·207. *Diphenylmethanephosphinous acid*, $CH_2Ph\cdot C_6H_4\cdot PHO\cdot OH$, is sparingly soluble in hot water, and when crystallised from alcohol melts at 84°; the *sodium*, *potassium*, *ammonium*, *barium*, *copper*, and *lead* salts have been analysed, and the *phenylhydrazine* salt melts at 171°. *Diphenylmethanephosphinic acid*, $CH_2Ph\cdot C_6H_4\cdot PO(OH)_2$, crystallises in long, silky, colourless needles, and melts at 196°; the *hydrogen potassium*, *ammonium*, *barium*, *hydrogen barium*, *cobalt*, *copper*, *lead*, and *silver* salts have been analysed, and the *phenylhydrazine* salt melts at 187°. *Phosphinodiphenylmethane*, $C_{13}H_{11}\cdot PO_2$, is a snow-white, crystalline powder which melts at 169°; water converts it slowly into the phosphinic acid. *Diphenylmethanephosphine*, $C_{13}H_{11}\cdot PH_2$, melts at 46° and boils at 184° under 20 mm. pressure; the *hydriodide* melts at 134°, and the *dimethyl* and *diethyl* derivatives boil at 197° and 235° under 20 mm. pressure respectively.

Benzophenonephosphinic acid, $COPh\cdot C_6H_4\cdot PO(OH)_2$, obtained by oxidising diphenylmethanephosphinic acid with potassium permanganate, crystallises in white, nacreous leaflets and melts at 204°; the *silver*, *ammonium*, and *lead* salts have been analysed, whilst the *phenylhydrazone* forms white, lustrous leaflets which melt at 124°. The *diethyl* ester of benzophenonephosphinic acid is a viscous oil having a pleasant odour; the *oxime* crystallises from absolute alcohol. *Di-*

phenyldichloromethaneoxychlorophosphine, $CCl_2Ph\cdot C_6H_4\cdot POCl_2$, prepared by the action of phosphorus pentachloride on benzophenonephosphinic acid, melts at 64°, and boils at 258° under 15 mm. pressure; it dissolves readily in ether, and is decomposed by water into benzophosphinic acid and hydrogen chloride.

[With Hugo Ciani].—*Dibenzylchlorophosphine*, $CH_2Ph\cdot CH_2\cdot C_6H_4\cdot PCl_2$, obtained from dibenzyl, phosphorus trichloride, and aluminium chloride, melts at 2°, and boils at 250° under 60 mm. pressure; the *tetrachloride* and *oxychloride* melt at 65° and 75° respectively. *Dibenzylphosphinous acid*, $C_{14}H_{13}\cdot PHO\cdot OH$, crystallises from dilute alcohol in transparent, nacreous leaflets, and melts at 156—157°; the *sodium* salt is sparingly soluble, and the *potassium*, *ammonium*, *lead*, *copper*, and *phenylhydrazine* salts are well defined. *Dibenzylphosphinic acid*,

$$CH_2Ph\cdot CH_2\cdot C_6H_4\cdot PO(OH)_2,$$

crystallises in lustrous, colourless leaflets, and melts at 256°; when strongly heated, the acid is resolved into dibenzyl and metaphosphoric acid, whilst oxidation converts it into benzoic and *p*-benzophosphinic acids. *Dibenzylphosphine*, $C_{14}H_{13}\cdot PH_2$, melts at 75°, and boils at 190° under 45 mm. pressure; the hydriodide is crystalline, and the alkyl derivatives are oils.

[With A. Buss].—*Diphenylchlorophosphine*, $C_6H_4Ph\cdot PCl_2$, prepared by heating diphenyl with phosphorus trichloride and aluminium chloride and distilling the product in an apparatus which is described and figured in the paper, melts at 5°, and boils at 200—220°; it has a sp. gr. 1·3098 at 14°. *Diphenylphosphinous acid*, $C_6H_4Ph\cdot PHO\cdot OH$, is a white, crystalline powder, forming well defined *potassium*, *calcium*, and *barium* salts.

[With Wilhelm Söchtig].—*Phenyl*-p-*tolylchlorophosphine*,

$$C_6H_4Me\cdot PPhCl,$$

prepared by heating mercury diphenyl with tolylchlorophosphine in a reflux apparatus at 270°, is a colourless oil which has an unpleasant smell, and boils at 340°. The *trichloride*, $C_6H_4Me\cdot PPhCl_3$, forms yellow crystals, and *phenyltolylphosphinic acid*, $C_6H_4Me\cdot PPhO\cdot OH$, crystallises in slender needles melting at 116°, and forming well-defined salts. *Dinitrophenyltolylphosphinic acid*,

$$NO_2\cdot C_6H_3Me\cdot P(C_6H_4\cdot NO_2)O\cdot OH,$$

crystallises from alcohol in small, yellow needles and melts at 205°; the *silver* salt is colourless. *Phenyltolylethylphosphine*, $C_6H_4Me\cdot PPhEt$, a colourless oil having an agreeable odour, boils at 340°; the *platinichloride* forms pale yellow needles. *Phenyltolylmethylethylphosphonium iodide* crystallises in long, slender needles and melts at 138°; the *platinichloride* crystallises in yellow needles. The *anilide* of phenyltolylphosphinous acid, $C_6H_4Me\cdot PPh\cdot NHPh$, obtained from phenyltolylchlorophosphine and aniline in benzene solution, crystallises from dilute alcohol in slender needles, and melts at 124°; the p-*toluidide* melts at 142°.

p-*Ditolylchlorophosphine*, $(C_6H_4Me)_2PCl$, is a colourless oil which boils at 345—350°; the *trichloride*, $(C_6H_4Me)_2PCl_3$, is crystalline, and the *oxychloride*, $(C_6H_4Me)_2POCl$, boils above 360°. p-*Ditolylphosphinic acid*, $(C_6H_4Me)_2PO\cdot OH$, crystallises from dilute alcohol in slender, colourless needles and melts at 135°; the *barium*, *lead*, *copper*, *silver*, and *phenylhydrazine* salts are well defined. *Dinitroditolylphosphinic acid*, $(NO_2\cdot C_6H_3Me)_2PO\cdot OH$, crystallises from alcohol in small, yellow needles, and melts at 194°. p-*Tolylbenzophosphinic acid*, $CO_2H\cdot C_6H_4\cdot P(C_6H_4Me)O\cdot OH$, prepared by oxidising ditolylphosphinic acid, forms a white, crystalline powder, which melts above 300°, and decomposes at higher temperatures into toluene, carbon, benzoic acid, and phosphoric acid.

[With PAUL SCHÖNHERR].—*Ditolylthiochlorophosphine*,

$$PS(C_6H_4Me)_2Cl,$$

obtained by the action of aluminium chloride on a mixture of toluene and phosphorus thiochloride, crystallises from glacial acetic acid in short, white needles, and melts at 96°; when heated with water at 130—140°, it yields the *anhydride* of ditolyloxythiophosphinic acid, $[PS(C_6H_4Me)_2]_2O$, which separates from alcohol in lustrous crystals melting at 165—166°. *Ditolylthiophosphinamide*, $PS(C_6H_4Me)_2\cdot NH_2$, separates from alcohol in hard, transparent crystals, and melts at 139°; the *anilide*, *phenylhydrazide*, *piperidide*, and *diethylamide*, melt at 152°, 135·5°, 134°, and 177—178° respectively. *Ethyl ditolylthiophosphinate*, $PS(C_6H_4Me)_2\cdot OEt$, melts at 41—42°; the *phenyl* ester, $PS(C_6H_4Me)_2\cdot OPh$, separates from alcohol in small crystals, and melts at 135°. *Ditolylmethylphospine*, $PMe(C_6H_4Me)_2$, is a colourless liquid which boils at 345°, and has a disagreeable odour.

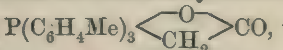
Tolylbenzylphosphinic acid, $C_6H_4Me\cdot P(CH_2Ph)O\cdot OH$, prepared by heating tolyldiphenol-*o*-phosphine with benzyl chloride at 170°, crystallises from alcohol in white, silky needles, and melts at 145°; the *phenyl* ester forms small, white crystals and melts at 120°.

[With H. HESS].—*Di-ψ-cumylchlorophosphine*, $(C_6H_2Me_3)_2PCl$, has not been obtained quite free from the primary derivative. *Phenyl-ψ-cumylchlorophosphine*, $C_6H_2Me_3\cdot PPhCl$, boils at 208° and 356° under 10 mm. and atmospheric pressures respectively; the *trichloride*, $C_{15}H_{16}\cdot PCl_3$, forms small, yellow crystals, and the *oxychloride*, $C_{15}H_{16}\cdot POCl$, is a liquid which boils at 210—215° under 10 mm. pressure. *Phenyl-ψ-cumylphosphinic acid*, $C_{15}H_{16}PO\cdot OH$, crystallises from alcohol in needles melting at 181°; the *phenylhydrazine* salt melts at 140·5°, and the *silver*, *copper*, and *cobalt* salts are well-defined. *Phenyltrinitro-ψ-cumylphosphinic acid*, $C_{15}H_{13}(NO_2)_3PO\cdot OH$, crystallises in yellow prisms and melts at 197—198°; the *silver* salt is amorphous. *Phenyl-ψ-cumylethylphosphine*, $C_{15}H_{16}PEt$, is a pale yellow, viscous liquid, which has a disagreeable smell, and boils at 225—230° and 352° under 10 mm. and atmospheric pressures respectively; the *mercurichloride* and *platinichloride* are crystalline, but the *methiodide* is an oil, forming a *platinichloride* which melts at 186°.

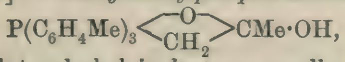
[With FELIX OHM].—*Tri-*p-*tolylphosphine*, $P(C_6H_4Me)_3$, prepared by the action of sodium on a mixture of *p*-bromotoluene and phosphorus trichloride in ether, crystallises from alcohol in white prisms and melts at 146°. *Tri-*p *tolylphosphine oxide*, $PO(C_6H_4Me)_3$, obtained by oxidising the phosphine with sodium hypobromite, crystallises in small needles and melts at 145°; the *trinitro*-derivative separates from alcohol in pale yellow needles and melts at 153°, whilst the *triamino*-derivative crystallises in aggregates of small needles containing 1 mol. of alcohol and melts at 235°.

Tri-p-*tolylphosphine sulphide*, $PS(C_6H_4Me)_3$, crystallises from alcohol in white, lustrous needles and melts at 182°. *Tri*-p-*tolylphosphine selenide*, $(C_6H_4Me)_3PSe$, separates from alcohol in snow-white, silky needles, and melts at 193°. *Tri*-p-*tolylmethylphosphonium iodide*, $PMe(C_6H_4Me)_3I$, crystallises from water in needles containing $1H_2O$, and from alcohol in prisms containing 1 mol. of the solvent; it melts at 108°. The *chloride* melts at 80°, and the *platinichloride* crystallises in reddish-yellow needles melting at 245°.

Di-p-*tolylmethylphosphine oxide*, $PMe(C_6H_4Me)_2O$, obtained by heating tritolylmethylphosphonium iodide with potassium hydroxide, crystallises from alcohol and melts at 143°. *Tri*-p-*tolylethylphosphonium iodide*, $PEt(C_6H_4Me)_3I$, crystallises from water or from alcohol in white, lustrous needles, and melts at 185°. *Tri*-p-*tolyl*-n-*propylphosphonium iodide*, $PPr^{a}(C_6H_4Me)_3I$, forms white needles and melts at 182°; *tri*-p-*tolyl*-iso*propylphosphonium iodide* and *tri*-p-*tolyl*iso*butylphosphonium iodide* melt at 184° and 104° respectively.

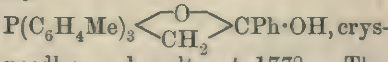
[With C. Hosseus].—*Ethyl tritolylphosphorbetaine hydrochloride*, $CO_2Et{\cdot}CH_2{\cdot}PCl(C_6H_4Me)_3$, is prepared by heating tritolylphosphine with ethyl chloroacetate at 70° (compare Michaelis and Köhler, Abstr., 1899, i, 596); sodium carbonate or hydroxide converts the salt into *tritolylphosphorbetaine*,  $P(C_6H_4Me)_3{<}\genfrac{}{}{0pt}{}{O}{CH_2}{>}CO$, which separates from ether in small, white crystals and melts at 145°.

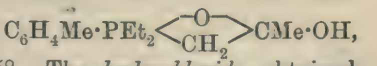
[With W. Krahe].—*Tritolylmethylphosphorketobetaine*,

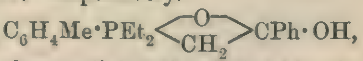


$$P(C_6H_4Me)_3{<}\genfrac{}{}{0pt}{}{O}{CH_2}{>}CMe{\cdot}OH,$$

crystallises from dilute alcohol in lustrous needles and melts at 107°. The *hydrochloride*, prepared by heating tritolylphosphine and chloroacetone at 85°, crystallises in aggregates of needles and melts at 245°; the *platinichloride*, *aurichloride*, *hydrobromide*, and *hydriodide* melt at 220°, 164°, 210°, and 189° respectively.

Phenyltritolylphosphorketobetaine,  $P(C_6H_4Me)_3{<}\genfrac{}{}{0pt}{}{O}{CH_2}{>}CPh{\cdot}OH$, crystallises in aggregates of lustrous needles and melts at 177°. The *hydrochloride*, or *tritolylphenacylphosphonium chloride*, prepared from tritolylphosphine and chloroacetophenone, melts at 226°; the *platinichloride*, *aurichloride*, *hydrobromide*, and *hydriodide*, melt at 240°, 156°, 248°, and 236° respectively.

Tolylmethyldiethylphosphorketobetaine,  $C_6H_4Me{\cdot}PEt_2{<}\genfrac{}{}{0pt}{}{O}{CH_2}{>}CMe{\cdot}OH$, is very hygroscopic, and melts at 75°. The *hydrochloride*, obtained from diethyltolylphosphine and chloroacetone, is an oil, but the *platinichloride* and *picrate* melt at 178° and 127° respectively.

Phenyltolyldiethylphosphorketobetaine,  $C_6H_4Me{\cdot}PEt_2{<}\genfrac{}{}{0pt}{}{O}{CH_2}{>}CPh{\cdot}OH$, is a colourless oil; the *hydrochloride* is also an oil, but the platinichloride crystallises in small, reddish-yellow needles, and melts at 173°.

[With Felix Ohm].—*Tribenzophosphinic acid*, $PO(C_6H_4{\cdot}CO_2H)_3$, prepared by oxidising tritolylphosphinoxide with chromic acid in acetic acid, forms a white, crystalline powder which melts at 247°, and sublimes when carefully heated; the *silver* salt is colourless.

[With L. EIFLER].—*Chlorophenyl*-p-*ditolylphosphine*,

$P(C_6H_4Me)_2\cdot C_6H_4Cl$,

produced by the action of sodium on an ethereal mixture of *p*-bromotoluene and chlorophenylchlorophosphine, separates from alcohol in colourless, highly refractive crystals melting at 115°. *Chlorophenyl*-p-*ditolylphosphine oxide*, $PO(C_6H_4Me)_2\cdot C_6H_4Cl$, crystallises from a mixture of benzene and petroleum in long, white needles and melts at 130°. *Chlorophenyl*-p-*ditolylphosphinesulphide*, $PS(C_6H_4Me)_2\cdot C_6H_4Cl$ and *chlorophenyl*-p-*ditolylphosphineselenide*, $PSe(C_6H_4Me)_2\cdot C_6H_4Cl$, melt at 149° and 172° respectively. *Chlorophenyl*-p-*ditolylmethylphosphonium iodide*, $PMe(C_6H_4Me)_2I\cdot C_6H_4Cl$, crystallises from water in long, broad needles containing $1H_2O$, and melts at 135°; the *chloride* crystallises with $4H_2O$, and melts at 72°, and the *platinichloride* melts and decomposes at 235°. *Chlorophenyl*-p-*ditolylethylphosphonium iodide*,

$PEt(C_6H_4Me)_2I\cdot C_6H_4Cl$,

forms needles which melt at 176·5°, and *chlorophenyl*-p-*ditolylbenzylphosphonium iodide*, $P(C_6H_4Me)_2(CH_2Ph)Cl\cdot C_6H_4Cl$, crystallises in leaflets which contain $2H_2O$ and melt at 257°.

Chlorophenyldibenzophosphinic acid, $PO(C_6H_4\cdot CO_2H)_2\cdot C_6H_4Cl$, obtained on oxidising ditolylchlorophenylphosphine oxide with chromic acid in acetic acid, crystallises in white leaflets.

[With M. HEINE.]—m-*Trixylylphosphine*, $P(C_6H_3Me_2)_3$, crystallises from alcohol in lustrous, white needles, and melts at 154°; the *mercurichloride* decomposes without fusion at 270°, and the *sulphide* crystallises in lustrous prisms melting at 167°. m-*Trixylylmethylphosphonium iodide*, m-*trixylylethylphosphonium iodide*, and m-*trixylylethylphosphonium platinichloride* melt at 230·5°, 225°, and 252° respectively.

[With ALFRED SCHAEUBLE].—p-*Trixylylphosphine*, $P(C_6H_3Me_2)_3$, crystallises from absolute alcohol in small, white, lustrous needles, and melts at 155°; the *mercurichloride* melts at 256°, whilst the *oxide* and *sulphide* melt at 173° and 170° respectively. p-*Trixylylmethylphosphonium iodide* and p-*trixylylethylphosphonium iodide* melt at 169° and 220° respectively.

[With D. VON KARCHOWSKI].—*Tri-ψ-cumylphosphine*, $P(C_6H_2Me_3)_3$, crystallises from a mixture of chloroform and petroleum in lustrous needles, and melts at 216—217°; the *oxide* and *sulphide* melt at 222° and 192° respectively. *Tri-ψ-cumylmethylphosphonium iodide* crystallises from alcohol in glistening leaflets and melts at 291°.

[With PAUL LOEBNER].—*Trimesitylphosphine*, $P(C_6H_2Me_3)_3$, separates as a white, crystalline powder, and melts at 205—206°. *Trimesitylmethylphosphonium iodide* melts at 269°. M. O. F.

Organic Chemistry.

Action of Aluminium Bromide on Chlorinated Acyclic Hydrocarbons. By Charles Pouret (*Bull. Soc. Chim.*, 1901, [iii], **25**, 293—299).— The preparation of bromine derivatives of methane by the action of aluminium bromide on the corresponding chlorine derivatives has already been described (Abstr., 1900, i, 369). The present paper describes the application of the method to the preparation of ethyl bromide, ethylene dibromide, ethylidene dibromide, acetylene tetrabromide, and pentabromoethane. In the action of aluminium bromide on ethyl chloride, a little ethylene is formed, but hydrogen bromide is not evolved. From this, and from the fact that ethyl bromide is scarcely acted on by aluminium chloride or bromide, it is concluded that the reaction consists in a simple substitution of bromine for chlorine, and not in the formation of ethylene and the fixation of hydrogen bromide by the latter. N. L.

Abnormal Behaviour of Polyhaloid Compounds with Alcoholic Potash. By Iwan L. Kondakoff (*J. pr. Chem.*, 1901, [ii], **63**, 113—140. Compare Abstr., 1899, i, 556, and this vol., i, 62).— The author combats the explanation given by Nef, Faworsky, and others of the syntheses effected by aluminium chloride, zinc chloride, &c., and maintains that the known additive products of hydrocarbons with aluminium chloride, &c., and not the methylene derivatives suggested by Nef, are the intermediate products in these reactions.

In the apparently abnormal behaviour of polyhaloid compounds with alcoholic potash, the author does not consider, with Nef, that a direct elimination of halogen occurs with the formation of methylene or acetylidene ($CH_2{:}C{:}$) derivatives, but rather holds that complicated reactions take place, in which the alcohol or potassium ethoxide in the alcoholic potash plays a part. Thus, in the conversion of tetramethylethylene dibromide into tetramethylethylene, hydrogen bromide is first eliminated in the normal manner, and di*iso*propenyl produced. The latter now unites with ethyl alcohol forming a compound $CMe_2Br{\cdot}CMe_2{\cdot}OEt$, which then decomposes into ethyl hypobromite and tetramethylethylene. K. J. P. O.

Action of Zinc on Tetramethylene Dibromide and Diiodide. By Jules Hamonet (*Compt. rend.*, 1901, **132**, 789—791).—The action of $\alpha\delta$-dibromobutane or $\alpha\delta$-diiodobutane on zinc in presence of alcohol yields butane, and not tetramethylene, and with zinc in the absence of alcohol, the product is ethylene. C. H. B.

Action of Zinc Dust on the Dibromides $C_nH_{2n}Br_2$. By Wladimir Ipatieff (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 151—154).— The action of zinc dust on $\alpha\gamma$-dibromo-γ-methylbutane yields γ-methyl-α-butene, together with an unsaturated bromide, C_5H_9Br, an unsaturated ethyl ether, $OEt{\cdot}C_5H_9$, and probably oxy-$\alpha\gamma$-dihydroxy γ-methylbutane. T. H. P.

Hexyl Bromide. By F. Bodroux (*Bull. Soc. Chim.*, 1901, [iii], **25**, 299—300).—A claim for priority as against Mouneyrat. N. L.

Chlorine Derivatives of the Hydrocarbons in California Petroleum. By Charles F. Mabery and Otto J. Sieplein (*Amer. Chem. J.*, 1901, **25**, 284—297. Compare Abstr., 1900, i, 533).—Chlorohexamethylene boils at 125·5°, and has the sp. gr. 0·9239 at 20°/4°, 0·9143 at 30°/4°, and 0·9044 at 40°/4°.

Chlorodimethylpentamethylene (?) distils at 147° and has a sp. gr. 0·9316 at 20°/4°. *Chloromethylhexamethylene* boils at 141—142°, and has a sp. gr. 0·9310 at 20°, the corresponding *nitrile* has a sp. gr. 0·9253 at 20°. When the chloro-derivative is treated with metallic sodium, a small amount of an unsaturated hydrocarbon boiling at 97°, with a double linking between a carbon atom of the side chain and one in the nucleus, is obtained. The *dibromide*, $C_7H_{12}Br_2$, derived from this has a sp. gr. 1·648 at 20°.

Chlorodimethylhexamethylene, $C_8H_{15}Cl$, boils at 168—170° and has a sp. gr. 0·9358 at 20°; the chlorine is probably contained in a side chain.

Chlorotrimethylhexamethylene, $C_9H_{17}Cl$, boils at 186—188° and has a sp. gr. 0·938 at 20°. When treated with sodium and dry ether, it yields an unsaturated *hydrocarbon*, C_9H_{16}, distilling at 135—140° and having a sp. gr. 0·7762 at 20°.

Chlorodecanaphthene, $C_{10}H_{19}Cl$, boils at 105—110° under 50 mm. pressure, and has a sp. gr. 0·947 at 20°. *Chloroundecanaphthene*, $C_{11}H_{21}Cl$, distils at 125—130° under 35 mm. pressure and has a sp. gr. 0·9583 at 20°. *Chlorododecanaphthene*, $C_{12}H_{23}Cl$, distils at 130—135° under 17 mm. pressure, and has a sp. gr. 0·9616 at 20°. *Chlorotridecanaphthene*, $C_{13}H_{25}Cl$, distils at 140—145° under 17 mm. pressure, and has a sp. gr. 0·9747 at 20°. *Chlorotetradecanaphthene*, $C_{14}H_{27}Cl$, distils at 150—155° under 13 mm. pressure, and has a sp. gr. 0·9748 at 20°/20°. *Chloropentadecanaphthene*, $C_{15}H_{29}Cl$, distils at 170—175° under 14 mm. pressure, and has a sp. gr. 0·9771 at 20°/20°.

All these chlorine derivatives have been obtained from the different hydrocarbons fractionated from California oils by passing chlorine into the oil floating on water. J. J. S.

Specific Gravities of Solutions of Three Substances: Alcohol, Ether, and Water. By W. I. Busnikoff (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 128—143).—The author has determined the sp. gr. at 15°/15° of a number of different mixtures of alcohol, ether, and water. On comparing the numbers obtained with those given by Squibb (*Zeit. anal. Chem.*, 1887, **26**), it is found that if one part of water be introduced into 100 parts of a mixture of alcohol and ether in any proportion, the sp. gr. of the mixture will be increased by about 0·002, the limiting numbers for the different mixtures being 0·001819 and 0·002334. On the basis of these observations, the following method is suggested for determining the composition of a mixture of alcohol, ether, and water. Firstly, the specific gravity is determined, after which the water present is completely removed by means of fused potassium hydroxide, and the sp. gr. of the resulting mixture of alcohol and ether also determined. The latter value, by reference to Squibb's table (*loc. cit.*) gives the proportions of ether and alcohol, whilst the difference between the sp. gr. before and after dehydration, divided by 0·002, gives the quantity of water referred to 100 parts of the ether-alcohol mixture.

Attention is called to the fact that mixtures of these three liquids which are saturated with respect to water have approximately molecular composition. Two such mixtures were examined, their compositions corresponding very nearly with the formulæ : $2EtOH + 4Et_2O + 3H_2O$ and $2EtOH + 5Et_2O + 3H_2O$. T. H. P.

Action of Octyl Alcohol on its Sodium Derivative. Synthesis of Di- and Tri-caprylic Alcohols. By Marcel Guerbet (*Compt. rend.*, 1901, **132**, 685—688. Compare Abstr., 1899, i, 471, 472, and this vol., i, 182).—The condensation taking place between the higher primary alcohols and their sodium derivatives also occurs in the case of the secondary alcohols. Octylic alcohol, when heated in contact with its sodium derivative at 200—250°, undergoes condensation, yielding two new alcohols and a trace of heptoic acid, the formation of the acid being accompanied by an evolution of hydrogen.

Dioctyl alcohol, separated from the other products by fractional distillation, is a colourless liquid having an odour resembling that of suet, it boils at 173° under 17 mm. pressure, and has the sp. gr. 0·8473 at 0° and 0·8387 at 15°.

Trioctyl alcohol, purified by conversion into its phthalic ester, is a colourless, oily liquid boiling at 227—230° under 12 mm. pressure ; its *acetic ester* boils at 224—227° under 10 mm. pressure. These compounds, like octyl alcohol itself, are both secondary alcohols, the esterification velocity of the dioctyl derivative being 20 ; amyl and heptyl alcohols give rise to primary alcohols, and these results indicate that in every case the condensation does not affect the carbon atom combined with the hydroxyl group. G. T. M.

Vaporisation and Hydration of Ethylene Glycol. By Robert de Forcrand (*Compt. rend.*, 1901, **132**, 688—690. Compare this vol., ii, 224).—The boiling points of ethylene glycol under varying pressures have been determined, and the data obtained employed in calculating the molecular heat of vaporisation at different temperatures, this quantity decreases slowly from 14·60 Cal. at 130·6° to 12·06 Cal. at 197°, the boiling point of the substance under 760 mm. pressure. The calculated vapour pressure of the glycol is 13·34 mm. at 100°, and 0·026 mm. at 10°. The compound is excessively hygroscopic, and in six weeks it absorbs 60 per cent. of water, this amount corresponding with the formation of the hydrate, $C_2H_6O_2,2H_2O$. The existence of this hydrate is also demonstrated thermochemically. The mean heat of hydration of glycol itself is 1·675 Cal., and it is found that the heats of hydration of mixtures of this substance with water, from $C_2H_6O,0·25H_2O$ to $C_2H_6O,2H_2O$, slowly decrease in accordance with the law expressed by the equation $Q = 1·675 - 0·260n$, but beyond this point they agree with the expression $Q = 1·202 - 0·147(n - 2)$, 1·202 being the heat of hydration of the dihydrate, and n the number of mols. of water. The following densities have been determined, $C_2H_6O_2$, 1·1297; $C_2H_6O_2,H_2O$, 1·17; $C_2H_6O_2,2H_2O$, 1·53, and $C_2H_6O_2,2·5H_2O$, 1·38, these data indicating that the formation of the dihydrate corresponds with the point of maximum contraction. The heat of formation of the dihydrate is 0·60 Cal. G. T. M.

Ethyl Hydroperoxide. By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1901, **34**, 738—749. Compare this vol., i, 62).—*Ethyl hydroperoxide*, EtO·OH, produced by shaking together a mixture of diethyl sulphate and excess of a 10 per cent. solution of hydrogen peroxide, is separated in the form of an oil by repeated distillation under ordinary and diminished pressures. The substance has not been obtained quite pure on account of its explosive nature; the product containing 80 per cent. of the compound boils at 47—49° under 100 mm., and at 95—100° under the ordinary pressure. It explodes when heated above its boiling point, or when mixed with "molecular" silver at the ordinary temperature; it has, however, no reducing action on silver oxide, and therefore differs from hydrogen peroxide, which reacts with silver oxide, but not with the finely divided metal.

Ethyl hydroperoxide is an acid the strength of which is comparable with that of phenol. The *sodium* and *potassium* salts show no tendency to crystallise, the *calcium* salt separates in readily soluble leaflets, the *barium* salt, $(C_2H_5O_2)_2Ba,2H_2O$, crystallises from water in lustrous prisms and from dilute alcohol in needles; it explodes on heating or by percussion, and is completely decomposed by carbon dioxide. Although the barium salt differs from barium peroxide in being readily soluble in water, yet it resembles the latter closely in other respects, and the authors accordingly assume that the compounds have constitutions corresponding with $Ba(O·OEt)_2$ and $Ba(O·O)_2Ba$ respectively. Ethyl hydroperoxide does not form salts with magnesia or with the hydroxides of the heavy metals; lead hydroxide, however, behaves exceptionally in yielding a white, unstable compound which rapidly becomes yellow. The reaction between "molecular" silver and ethyl hydroperoxide is moderated by the presence of water, and a dilute solution of the peroxide yields ethyl alcohol, acetaldehyde, alcohol, and oxygen; the action of the metal is almost wholly catalytic, although a certain amount undergoes oxidation. The peroxide oxidises mercury, its vapour blackening the metal, whilst the solution oxidises it to the black or yellow oxide or to white crystals. Platinum, zinc, aluminium, or magnesium in a finely-divided condition and red phosphorus are not oxidised by the peroxide; this substance slowly decolorises solutions of permanganic acid, but is without action on chromic, molybdic, or titanic acids. Hydrogen iodide and sulphide are both decomposed by the peroxide; sulphurous acid is converted into a mixture of sulphuric and ethyl sulphuric acids, whilst nitrous acid or ethyl nitrite yields ethyl nitrate. Amyl nitrite is resolved into ethyl nitrate and amyl alcohol.

The acyl chlorides and anhydrides, when treated with aqueous or alkaline solutions of the peroxide, yield the ethyl salts of the corresponding peracids. Acetic anhydride furnishes an oily product, probably ethyl peracetate, terephthalic chloride gives rise to *ethyl perterephthalate*, $C_6H_4(CO_3Et)_2$, a compound crystallising from benzene in plates melting at 37° and exploding at higher temperatures or on percussion; the new substance behaves more like an anhydride than an ester, being hydrolysed by aqueous alkalis into ethyl hydroperoxide and terephthalic acid. Ethyl piperidine oxide (Wolffenstein, Abstr., 1898, i, 536) is produced by the action of an aqueous solution of the peroxide on ethyl piperidine; primary and secondary bases are also attacked by the oxidising agent, but the products are indefinite.

Methyl hydroperoxide, an extremely explosive substance boiling at a lower temperature than its ethyl homologue, is produced, together with gaseous *dimethyl peroxide*, by the action of alkaline hydrogen peroxide solution on dimethyl sulphate. *Barium methyl hydroperoxide* crystalling in lustrous needles on adding alcohol to its concentrated aqueous solution, explodes when dry on trituration even at the ordinary temperature. G. T. M.

Nitrous Acid. By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1901, **34**, 755—762).—*Benzyl nitrite*, readily prepared by mixing together benzyl alcohol and sodium nitrite in a dilute sulphuric acid solution, is a pale yellow liquid boiling at 80—83° under 35 mm. pressure. It rapidly decomposes on keeping, with the formation of nitrous fumes and benzaldehyde. The compound described by Hollemann as benzyl nitrite boils 55° higher than the authors' compound (compare Abstr., 1895, i, 455). Hydrogen peroxide, in dilute solutions, oxidises nitrous acid quantitatively to nitric acid, and decomposes the alkyl nitrites, yielding the corresponding alcohols and traces of their aldehydes. Ethyl hydroperoxide oxidises nitrous acid and ethyl nitrite to the corresponding nitrate; amyl nitrite, under these conditions, yielding amyl alcohol and an oil boiling at 85—90° and burning with a white flame. These reactions are readily explained on the assumption that the reagent acting on nitrous acid or its ester first forms an additive compound, in which the nitrogen atom is quinquevalent, the final product resulting from the elimination of water or an alcohol, and the formation of a derivative of tervalent nitrogen. G. T. M.

Addition of Hydrogen Fluoride to Salts of Ethyl Sulphuric Acid and certain Sulphonic Acids. By RUDOLPH F. WEINLAND and G. KAPPELLER (*Annalen*, 1901, **315**, 357—378. Compare Abstr., 1899, ii, 594).—The potassium and rubidium salts of certain organic derivatives of sulphuric acid combine with hydrogen fluoride when treated with aqueous solutions of this acid; this property, which is shared by some of the analogous cæsium derivatives, is altogether wanting in the corresponding salts of sodium, ammonium, and the bivalent metals. The free sulphonic acids, excepting sulphanilic acid, which may be regarded as an internal salt, do not, under these conditions, combine with hydrogen fluoride. These additive compounds do not contain water of crystallisation.

Potassium ethyl sulphate, when treated with 40 per cent. hydrofluoric acid, yields the additive *compound*, $KEtSO_4,HF$, crystallising in colourless needles; the corresponding rubidium *salt* is more soluble and requires for its formation 65 per cent. hydrofluoric acid; the cæsium double salt could not be freed from the mother liquor.

Potassium ethanesulphonate and hydrofluoric acid yield an uncrystallisable syrup, whilst taurine does not combine with hydrogen fluoride. The additive compounds of potassium methyl and propyl sulphates could not be isolated, and potassium phenyl sulphate is decomposed by hydrofluoric acid even at the ordinary temperature. The *double* salts, $C_6H_5{\cdot}SO_3K,2HF$ and $C_6H_5{\cdot}SO_3Rb,2HF$, produced by the action of 40—60 per cent. hydrofluoric acid on the corresponding benzenesulphonates, crystallise in needles.

The *compound* $C_6H_4Me{\cdot}SO_3K,HF$, prepared from potassium *o*-toluenesulphonate, is fairly stable in air, and its crystallographic measurements show that it is not isomorphous with the hydrated salt $C_6H_4Me{\cdot}SO_3K,H_2O$, the former crystallising in the monoclinic system, the latter in the rhombic.

Potassium-*p*-toluenesulphonate yields two hydrogen fluoride *compounds*, $C_6H_4Me{\cdot}SO_3K,HF$ and $C_6H_4Me{\cdot}SO_3K,2HF$, the former produced in a 40 per cent. solution of hydrofluoric acid, the latter obtained when the concentration is at least 65 per cent.; they both crystallise in prisms resembling potassium nitrate. The *double* salts,

$$OH{\cdot}C_6H_4{\cdot}SO_3K,HF$$

and $OH{\cdot}C_6H_4{\cdot}SO_3K,2HF$, were obtained in a similar manner from potassium *p*-phenolsulphonate; only the *monohydrofluoride* could be isolated in the case of the rubidium salt; the corresponding cæsium *compound*, $OH{\cdot}C_6H_4{\cdot}SO_3Cs,HF$, crystallises in transparent, prismatic needles. Sulphosalicylic acid does not itself combine with hydrogen fluoride, but its potassium and rubidium salts yield with this reagent the following derivatives: $OH{\cdot}C_6H_3(CO_2H){\cdot}SO_3K,HF$,

$$OH{\cdot}C_6H_3(CO_2H){\cdot}SO_3K,2HF,$$

and $C_6H_3(OH)(CO_2H){\cdot}SO_3Rb,HF$. The formation of the *compound* $NH_2{\cdot}C_6H_4{\cdot}SO_3H,2HF$ from sulphanilic acid and 65 per cent. hydrofluoric acid is accompanied by a development of heat; the substance separates from the cooled solution in rhombic crystals which rapidly become turbid and decompose; it may also be produced by action of hydrogen fluoride on potassium sulphanilate. G. T. M.

Direct Nitration in the Aliphatic Series. By A. Wahl (*Compt. rend.*, 1901, **132**, 693—695. Compare this vol., i, 4).—The *compound* $C_6H_9O_4N$, produced in small quantity by the action of a mixture of nitric and sulphuric acids on ethyl crotonate at temperatures below 25°, boils at 100—106° under 13 mm. pressure. The ester employed in this experiment was prepared by boiling for several hours a mixture of ethyl bromobutyrate and diethylaniline, the yield being 40—50 per cent. of the theoretical (compare Bischoff, Abstr., 1899, i, 201). The ethyl salts of tiglic and *iso*lauronolic acid do not yield nitro-derivatives on treatment with nitric acid, the latter ester giving rise to a nitrate, $C_{11}H_{18}O_2,HNO_3$, crystallising in colourless prisms and melting at 79°.

G. T. M.

Adamkiewicz's Proteid Reaction, Chemistry of Glyoxylic Acid. By F. Gowland Hopkins and Sidney W. Cole (*Proc. Roy. Soc.*, 1901, **68**, 21—33).—The proteid reaction described by Adamkiewicz (Abstr., 1875, 172) is very uncertain; with some specimens of acetic acid little or no coloration is produced. The authors have found that the colour change which occurs is not due to furfuraldehyde, as suggested by Udranszky (Abstr., 1888, 863), but to glyoxylic acid, small quantities of which are usually present in acetic acid. If a specimen of glacial acetic acid which yields the reaction is distilled, the glyoxylic acid collects in the earlier fractions, and the residue gives no coloration with proteid and sulphuric acid.

When acetic acid is heated with hydrogen peroxide in presence of ferrous iron, glyoxylic acid is produced, but is largely converted into formaldehyde. Glyoxylic acid is slowly formed when acetic acid is left exposed to the air and more rapidly in presence of ferrous iron and under the influence of direct sunlight.

Glycol, glycollaldehyde, glycollic acid, oxalic acid, and pyruvic acid do not yield the Adamkiewicz reaction, which appears to be peculiar to glyoxylic acid. If the acetic acid is replaced by an aqueous solution of glyoxylic acid, the test becomes trustworthy; a solution suitable for the purpose is readily prepared by reducing a solution of oxalic acid with sodium amalgam. The proteid or proteid solution to be tested is first added to the reagent, and then strong sulphuric acid poured down the side of the test-tube; a brilliant violet-blue colour is produced at the junction of the liquids. E. G.

Synthesis and Properties of α-Dimethyl-β-ethylhydracrylic Acid. By B. Schischkowsky and Sergius N. Reformatsky (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 158—163).—*αα-Dimethyl-β-ethylhydracrylic* [*β-hydroxy-αα-dimethylvaleric*] *acid*, $CO_2H·CMe_2·CHEt·OH$, obtained by the action of zinc on a mixture of equivalent proportions of propaldehyde and ethyl α-bromo*iso*butyrate, crystallises from acetic acid in hexagonal plates and from water in large prisms melting at 103°. It has the normal molecular weight in freezing acetic acid and its mean electrical conductivity constant is K 0·00150, the mean value for β-hydroxy-acids being 0·00180. The *sodium*, *calcium*, *lead*, *silver*, *zinc*, and *barium* salts were prepared. When distilled, the acid undergoes decomposition into propaldehyde and *iso*butyric acid, whilst under the action of hydriodic or sulphuric acid, it yields a lactone, $C_7H_{12}O_2$, melting at 52°, previously obtained by Anschütz and Gillet (Abstr., 1888, 1272). T. H. P.

Action of Butyryl Chloride on Methyl Sodioacetoacetate. By Louis Bouveault and A. Bongert (*Compt. rend.*, 1901, **132**, 701—704. Compare Abstr., 1900, i, 474).—The action of acid chlorides on the sodium derivatives of the alkyl esters of acetoacetic acid results in the formation of two isomeric esters (compare Claisen, *Annalen*, 1897, **297**, 2); the one corresponding with the ketonic form of the ester is indicated by the symbol C, and the other by the prefix O.

Methyl butyrylacetoacetate (C-ester), $CPr^{\alpha}O·CHAc·CO_2Me$, produced by adding butyryl chloride to methyl sodioacetoacetate suspended in dry ether, is separated from the isomeric ester by means of a saturated solution of sodium carbonate in which the latter is insoluble; it is a colourless, slightly odorous liquid, boils at 105° under 14 mm. pressure, has a sp. gr. 1·0978 at 0°, and develops a coloration with ferric chloride. The *copper* derivative forms small blue crystals soluble in alcohol, chloroform, or ether, but insoluble in light petroleum; the *sodium* derivative is a white, microcrystalline powder soluble in water and alcohol. The isomeric O-ester, *methyl β-butyryloxycrotonate*,

$$Pr^{a}CO\cdot OCMe\dot{:}CH\cdot CO_2Me,$$

is a colourless liquid boiling at 104—105° under 10 mm. pressure; it yields no metallic derivatives and does not develop a coloration with ferric chloride.

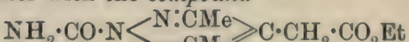
The O-ester is not attacked by water even in sealed tubes at 140—150°. The C-isomeride, on the other hand, is readily hydrolysed in boiling aqueous solutions into methyl alcohol, carbon dioxide, and butyrylacetone (Claissen and Ehrhardt, Abstr., 1889, 850); it is also decomposed by the alkali hydroxides into acetic acid and *methyl butyrylacetate*; the latter compound, under these conditions, undergoes further hydrolysis, but is, however, obtained in a state of purity by the employment of ammonia and sodium methoxide as hydrolytic agents. Methyl butyrylacetate, a colourless liquid with a fruity odour, boils at 85° under 14 mm. pressure and has a density 1·037; its *copper* derivative melts at 128°.

Methyl β-butyryloxycrotonate is only slowly attacked by aqueous potassium hydroxide solution; the hydrolysis, however, proceeds more rapidly on heating, the products being methyl alcohol and potassium acetate and butyrate; when treated with an ethereal ammonia solution, the ester yields methyl acetoacetate and butyramide.

Methyl "dibutyrylacetoacetate," $COPr^{a}\cdot O\cdot CMe\dot{:}C(COPr^{a})\cdot CO_2Me$, is formed in small amount in the preceding condensation; it is a yellowish liquid and boils at 146° under 10 mm. pressure.

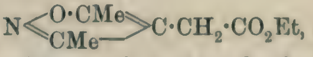
Methyl acetoacetate, when treated with ammonia gas, yields a trace of methyl β-aminocrotonate. G. T. M.

Ethyl Diacetylpropionate. By F. March (*Compt. rend.*, 1901, 132, 697—699. Compare Abstr., 1900, i, 374).—The *disemicarbazone*, $CH(CMe\dot{:}N\cdot NH\cdot CO\cdot NH_2)_2\cdot CH_2\cdot CO_2Et$, of ethyl ββ-diacetylpropionate is produced together with the *compound*

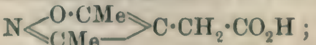


$$NH_2\cdot CO\cdot N\!<\!\begin{matrix}N\dot{:}CMe\\ \text{——}CMe\end{matrix}\!>\!C\cdot CH_2\cdot CO_2Et$$

by the action of semicarbazide hydrochloride on the ester in the presence of sodium acetate; the two compounds are separated by extraction with ether, the latter dissolves and separates from the solvent in colourless crystals melting at 121—122°, whilst the former is very slightly soluble in the ordinary organic solvents and melts at 224—225°.

The *oxazole*,  $N\!<\!\begin{matrix}O\cdot CMe\\ CMe\text{——}\end{matrix}\!>\!C\cdot CH_2\cdot CO_2Et$, obtained by heating on the water-bath a mixture of hydroxylamine hydrochloride, potassium carbonate, and ethyl ββ-diacetylpropionate, is an oil boiling at 152° under 25 mm. pressure; it is insoluble in water but miscible with ether or alcohol.

Alkaline hydrolysis of the preceding ester yields a solution of an alkali salt which, when acidified, furnishes the *acid*



$$N\!<\!\begin{matrix}O\cdot CMe\\ CMe\text{——}\end{matrix}\!>\!C\cdot CH_2\cdot CO_2H\,;$$

this crystallises in needles melting at 122° and is readily dissolved in water, alcohol, or ether. The *barium* salt, $Ba(C_7H_8O_3N)_2,2H_2O$, crystallises in needles soluble in water or alcohol and melts at 196—198°; the *cupric* and *silver* salts are obtained as green and white precipitates respectively, the *alkali* salts are very soluble and deliquescent. All attempts to obtain ββ-diacetylpropionic acid have proved of no avail, the ester on alkaline hydrolysis yielding a mixture of acetic and lævulic acids. G. T. M.

Osmyloxalates. By L. Wintrebert (*Compt. rend.*, 1901, **132**, 824—826. Compare Abstr., 1900, i, 543).—Sodium osmyloxalate, $OsO_2(C_2O_4)_2Na_2,2H_2O$, may be produced by Vèzes' method from oxalic acid and an alkaline solution of osmium tetroxide, but is more easily prepared by treating the peroxide with a solution of oxalic acid and sodium hydrogen oxalate; the salt separates from concentrated solutions in reddish-brown crystals.

Ammonium osmyloxalate, $OsO_2(C_2O_4)_2(NH_4)_2,2H_2O$, produced by heating at 80° for three weeks a concentrated solution of osmium tetroxide and ammonium hydrogen oxalate, separates in well-defined red crystals. In this preparation, the use of ammoniacal solutions must be avoided, since the ammonia reduces the peroxide, forming ammonium osmiamate, $NH_4O{\cdot}OsO{\cdot}NO$. The *silver* salt, $OsO_2(C_2O_4)_2Ag_2$, formed from silver nitrate and an alkali osmyloxalate, is employed in the preparation of the corresponding salts of the alkaline earth metals from their chlorides. The *barium* salt, $OsO_2(C_2O_4)_2Ba,4H_2O$, crystallises in greenish-yellow needles; the *strontium* and *calcium* salts are unstable, greenish-yellow powders, having a similar composition, the former crystallising with $4H_2O$ and the latter with $2H_2O$. An abnormal *barium* salt, $OsO_2(C_2O_4)_3Ba_2,6H_2O$, produced by warming a solution of potassium or barium osmyloxalate, oxalic acid, and barium chloride, separates on cooling in yellowish-brown crystals.

G. T. M.

Properties of Acyl Derivatives of Ethyl Cyanoacetonedicarboxylate. Action of Cyanogen Chloride on Methyl Acetonedicarboxylate. By Juvénal Derôme (*Compt. rend.*, 1901, **132**, 699—701. Compare Abstr., 1900, i, 426).—The *compound* $NH_2{\cdot}CO{\cdot}C(CN){\vdots}C(NH_2){\cdot}CH_2{\cdot}CO_2Et$ is obtained as a white, crystalline precipitate melting at 195° by the action of aqueous ammonia on ethyl cyanoethylacetonedicarboxylate. The formula given to this product corresponds with the enolic form of the parent ester; this view of its constitution is confirmed by the fact that the same substance is produced from the methyl and propyl derivatives of ethyl cyanoacetonedicarboxylate.

Ethyl cyanomethylacetonedicarboxylate,

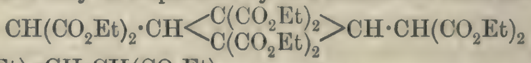
$$CO_2Et{\cdot}C(CN){\vdots}C(OMe){\cdot}CH_2{\cdot}CO_2Et,$$

prepared by the action of methyl iodide on the silver derivative of ethyl cyanoacetonedicarboxylate suspended in ether, separates from this solvent in transparent crystals and melts at 70°; it is slightly soluble in water but readily dissolves in chloroform.

Ethyl cyanopropylacetonedicarboxylate crystallises in colourless needles and melts at 20°; it resembles its lower analogue, and is prepared in a similar manner.

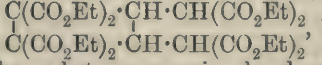
Methyl cyanoacetonedicarboxylate, $\mathrm{CO_2Me{\cdot}CH(CN){\cdot}CO{\cdot}CH_2{\cdot}CO_2Me}$, produced by the action of cyanogen chloride on the sodium derivative of methyl acetonedicarboxylate, melts at 64°; its *copper* derivative is soluble in alcohol or chloroform, separates from solution in green crystals, and melts at 145°. G. T. M.

Bimolecular Ethyl Dicarboxyglutaconate. By MAX GUTHZEIT and A. WEISS (*Ber.*, 1901, **34**, 675—680. Compare Abstr., 1899, i, 115).—When a benzene solution of ethyl dicarboxyglutaconate (16 mols.) is left in contact with piperidine (1 mol.) at the ordinary temperature for some time, well developed rhombohedra of a *bimolecular ester*, $\mathrm{C_{30}H_{44}O_{16}}$, melting at 102—103°, are deposited. When this is hydrolysed with dilute acids, a *bimolecular dicarboxyglutaconic acid* melting at 234° is obtained, but when hydrolysed with potassium hydroxide the ordinary unimolecular acid melting at 137° is formed. An isomeric bimolecular ester melting at 87—88° is obtained when a 15 per cent. benzene solution of the ester melting at 102—103° is left in contact with an excess of piperidine. Both esters are converted into the oily unimolecular esters when treated with sodium ethoxide and then with dilute acids, and both appear to be saturated compounds and do not give the ordinary enolic reactions. The isomerism for the two new esters may be explained by the structural formulæ



$$\mathrm{CH(CO_2Et)_2{\cdot}CH}<\begin{matrix}\mathrm{C(CO_2Et)_2}\\ \mathrm{C(CO_2Et)_2}\end{matrix}>\mathrm{CH{\cdot}CH(CO_2Et)_2}$$

and



$$\begin{array}{l}\mathrm{C(CO_2Et)_2{\cdot}CH{\cdot}CH(CO_2Et)_2}\\ \;| \qquad\qquad\;\; |\\ \mathrm{C(CO_2Et)_2{\cdot}CH{\cdot}CH(CO_2Et)_2}\end{array}$$

, but stereoisomerism is also possible.

The substance previously described as the ketonic form of ethyl *iso*aconitate is now shown to be a bimolecular ester, as on hydrolysis it yields von Pechmann's bimolecular glutaconic acid melting at 207° (Abstr., 1899, i, 870). J. J. S.

Velocities of Formation and Decomposition of Methylal at the Ordinary Temperature. By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1901, [iii], **25**, 364—369).—The results of the author's experiments on the formation and decomposition of methylal (this vol., i, 254) are submitted to mathematical analysis, from which, however, no definite conclusions as to the mechanism of the reactions can be drawn, various different hypotheses being equally valid. N. L.

Heats of Formation of Acetals and their Isomerides. By MARCEL DELÉPINE (*Compt. rend.*, 1901, **132**, 777—779).—Comparison of the heats of formation of methylal and propylglycol, acetal and pinacone, glycol formal and propionic acid, glycol acetal and butyric acid, erythritol diformal and adipic acid, erythritol diacetal and suberic acid, mannitol triformal, and the homologue of tricarballylic acid (calculated) shows that the difference between a formal and the isomeric acid varies from 2 × 21 Cal. to 4 × 18·9 Cal., and 6 × 17 Cal., seemingly becoming less as the number of ·O· linkings increases. With acetals, the values are somewhat lower, but are of the same order.

The heat of combustion of β-naphthol formal is 8335·6 cal., its molecular heat of combustion 2500·7 cal. at const. vol. and 2502·4 cal. at const. pressure, and its heat of formation 29·9 Cal., whilst the corresponding values for β-dinaphthylolmethane, $CH_2[C_{10}H_6(OH)]_2$, are 8252·2 cal., 2475·7 cal. and 2477·4 cal., and 54·9 Cal. The difference is therefore 2 × 12·5 Cal. It follows that

$$CH_2O \text{ diss.} + 2C_{10}H_7{\cdot}OH \text{ sol.} = \begin{cases} CH_2[C_{10}H_6(OH)]_2 \text{ sol.} + H_2O \text{ liq. develops } +26{\cdot}1 \text{ Cal.} \\ CH_2(OC_{10}H_7)_2 \text{ sol.} + H_2O \text{ liq.} \quad \text{,,} \quad +\ 1{\cdot}1 \text{ ,,} \end{cases}$$

The formation of the formal is not reversible, but if the compound is heated at 100° with absolute alcohol containing a small quantity of hydrochloric acid it is converted into its isomeride. C. H. B.

Oxycelluloses. By A. Nastukoff (*Ber.*, 1901, **34**, 719—723).—When either of the oxycelluloses formerly described (Abstr., 1900, i, 540) is heated on the water-bath for 1—3 hours with 5 per cent. sulphuric acid, and after washing with water, with 10 per cent. aqueous sodium hydroxide for 10—30 minutes at 70—100°, it becomes easily soluble in water, especially at 100°; heating with alkali alone is insufficient, and the sulphuric acid must be of greater concentration than 1 per cent. The oxycellulose prepared with permanganate requires to be heated for only 1 hour with the acid, but that obtained with bleaching powder requires 3 hours. The 5—10 per cent. aqueous solutions obtained are as viscous as glycerol, and when evaporated on glass give lustrous, easily stripped, transparent films; they are not changed by keeping or boiling, yield precipitates with many mineral salts (for example, sodium chloride, barium chloride) and in this respect resemble Guignet's colloidal cellulose (Abstr., 1889, 847). From this they differ, however, by reducing Fehling's solution and yielding yellow compounds with phenylhydrazine. On adding an acid to the aqueous solutions of the modified oxycelluloses, a precipitate is obtained which, if kept moist, can be redissolved, but if dried in the air, or washed with a weak acid, becomes insoluble; the solubility is restored, however, by heating with 10 per cent. aqueous sodium hydroxide. The phenylhydrazone prepared from the oxycellulose which has been rendered insoluble, is itself insoluble, but changes to the soluble form when heated with the alkali; the phenylhydrazone of the soluble oxycellulose, however, is directly soluble in water. As the soluble oxycelluloses contain a small quantity of combined alkali, they are probably the sodium salts of acids, which are themselves soluble in water but become converted into insoluble anhydrides or lactones on drying; the insoluble precipitates formed on adding iron, copper, and similar salts to the solutions of the oxycelluloses are probably insoluble salts of these acids. In empirical composition, the soluble oxycelluloses hardly differ from the original α-oxycellulose. They are not coloured by iodine, and do not give the phloroglucinol reaction in presence of hydrochloric acid.

β-Oxycellulose, obtained by the oxidation of cellulose with nitric acid, when heated with aqueous sodium hydroxide alone without preliminary treatment with sulphuric acid, becomes soluble in water, but the solutions obtained, although similar to those from α-oxycellulose, dry on to glass in the form of a hard, firmly-adhering film which, when removed, breaks up into a dull powder. The new, soluble substances are therefore not identical with β-oxycellulose, and to distinguish them they are provisionally termed γ-*oxycelluloses*.

W. A. D.

Formation of Secondary *s*-Acid Hydrazides. By Robert Stollé (*Ber.*, 1901, **34**, 681—682. Compare Abstr., 1899, i, 413, and Autenrieth and Spiess, this vol., i, 230).—A very good method for the preparation of secondary *s*-acid hydrazides is to heat the primary hydrazides with acid anhydrides to a fairly high temperature.

s-Dibutyrylhydrazide melts at 167°, not at 162—163°, distils at 214° under 24 mm. pressure, and is insoluble in dry ether. Dibenzoylhydrazide melts at 238°, and not at 233°.

J. J. S.

Action of Acid Chlorides and Anhydrides on the Organometallic Compounds of Magnesium. By Tissier and Victor Grignard (*Compt. rend.*, 1901, **132**, 683—685. Compare this vol., i, 250).—The acid chlorides and anhydrides of the organic acids react very violently with the magnesium alkyl iodides, and in practice the reagents are diluted with ether and cooled with ice. The action takes place in two stages, the addition of 1 mol. of magnesium methyl iodide to acetyl chloride giving rise to the substance $CMe_2Cl\cdot OMgI$, whilst a second mol. of the organometallic iodide furnishes the final product $CMe_3\cdot OMgI$, this compound, on treatment with water, yielding trimethylcarbinol. When acetic anhydride is employed, the intermediate product has the composition $OAc\cdot CMe_2\cdot OMgI$, the final result being the same as in the preceding example. When benzoyl chloride or oxide is substituted for its acetic analogue, a similar series of reactions gives rise to phenyldimethylcarbinol; this compound, formerly described as a liquid, is, in reality, a solid melting at 23° and boiling at 89—90° under 10 mm. pressure (compare Abstr., 1900, i, 382). The alcohol, when distilled under the ordinary pressure, decomposes into water and β-phenylpropylene, $CMePh\colon CH_2$, an olefine boiling at 158—160° under 8 mm. pressure.

G. T. M.

Organometallic Compounds of Magnesium. By Tissier and Victor Grignard (*Compt. rend.*, 1901, **132**, 835—837. Compare Abstr., 1900, i, 382).—The saturated hydrocarbons may be prepared in a state of purity by dropping a mixture of ether and water on to the magnesium alkyl haloids maintained at 0°. When an alkyl haloid is added to magnesium, two reactions occur, one involving the formation of the corresponding magnesium alkyl haloid, and the second, which gives rise to a higher hydrocarbon, taking place in accordance with the following equation,

$$2C_nH_{2n+1}M + Mg = MgM_2 + (C_nH_{2n+1})_2,$$

where M is the halogen radicle. The second reaction, which takes place only to a limited extent among the lower members of the series, becomes more pronounced as the alkyl radicle involved increases in complexity. At the C_6 term both actions take place to the same extent. Magnesium decomposes ethylene dibromide, causing the evolution of ethylene; a similar reaction takes place with other haloid compounds containing 2 atoms of the halogen. When an alcohol is added to a magnesium alkyl haloid, the following reaction occurs, $C_nH_{2n+1}MgM + R^IR^{II}R^{III}C\cdot OH = C_nH_{2n+2} + R^IR^{II}R^{III}\cdot CO\cdot MgM$. The new organometallic derivatives are obtained crystalline; they are decomposed by water, regenerating the alcohol. Phenol and methyl, ethyl, and amyl alcohols react in this manner with magnesium ethiodide.

Magnesium readily dissolves in methyl alcohol, forming magnesium methoxide, $Mg(OMe)_2$, a white substance readily decomposed by water; the metal is not very soluble in ethyl alcohol, even at its boiling point, the ethoxide being formed, however, when the reaction is carried out in sealed tubes. G. T. M.

Action of the Esters of Dibasic Acids on Organometallic Compounds. By Amand Valeur (*Compt. rend.*, 1901, **132**, 833—834. Compare this vol., i, 246, 249).—The author has applied the Wagner-Saytzeff reaction to esters of the oxalic acid series. The pinacone of acetone results from the interaction of magnesium methiodide and ethyl oxalate. Ethyl malonate, when treated with magnesium ethiodide, yields an unsaturated *alcohol*, $C_{11}H_{22}O$, boiling at 177—178°; this compound is probably formed by the dehydration of the glycol, $OH\cdot CEt_2\cdot CH_2\cdot CEt_2\cdot OH$.

The *glycol*, $OH\cdot CEt_2\cdot CH_2\cdot CH_2\cdot CEt_2\cdot OH$, prepared from ethyl succinate and magnesium ethiodide, crystallises from benzene and melts at 70°. G. T. M.

New Reactions of Organometallic Compounds of Magnesium. By Charles Moureu (*Compt. rend.*, 1901, **132**, 837—839. Compare preceding abstracts).—Amyl nitrite and nitroethane, when treated with magnesium ethiodide, yield products which, on treatment with water, give rise to diethylhydroxylamine. Methyl nitrate interacts violently with magnesium methiodide, the product, when treated with water, yielding a basic substance boiling at 95°, and having the properties of a hydroxylamine derivative, probably dimethylhydroxylamine. G. T. M.

Ethereal Derivatives of the Organometallic Compounds. By Edmond E. Blaise (*Compt. rend.*, 1901, **132**, 839—841. Compare Grignard, Abstr., 1900, i, 382).—When an alkyl haloid reacts with magnesium in the presence of dry ether, a substance is formed containing the elements of the solvent, the *compounds*, $Et\cdot MgI,Et_2O$ and $Et\cdot MgBr,Et_2O$, being obtained from ethyl iodide and ethyl bromide respectively. The latter of these substances is remarkably stable, and does not lose its ether even at 145°.

These compounds form crystalline derivatives with certain nitriles, the products still containing the elements of ether; the following substances of this type have been prepared: $CEtPh\colon N\cdot MgI,Et_2O$, $CEtPh\colon N\cdot MgBr,Et_2O$, and $C_6H_4Me\cdot CEt\colon N\cdot MgI,Et_2O$.

Ether plays an essential part in the formation of organometallic magnesium compounds, and the reaction between the metal and the alkyl iodide does not take place when this solvent is replaced by some other medium. G. T. M.

The Benzene Ring System. By Hugo Kauffmann (*Ber.*, 1901, **34**, 682—698. Compare Abstr., 1900, i, 480).—It is shown by reference to numerous specific examples that those benzene compounds which, in the form of vapour, are capable of absorbing Tesla rays and transforming them into violet light are also the compounds which have been shown by Perkin (Trans., 1896, **69**, 1025) to possess abnormal molecular magnetic rotation.

The magnetic rotations of all such substances are much higher (in some cases even 100 per cent.) than those calculated from the sum of the atomic rotations, and it is exactly those compounds which give highly luminous vapours which possess the greatest abnormality. The same compounds also appear to have abnormally high molecular refraction, and still higher molecular dispersion, coefficients.

J. J. S.

Electrolytic Oxidation of Toluene. By Karl Puls (*Chem. Zeit.*, 1901, **25**, 263).—The experiments were similar to those of Merzbacher and E. F. Smith (this vol., i, 134), and gave similar results. Benzaldehyde, ethyl benzoate, and *p*-sulphobenzoic acid were obtained; of benzoic acid itself, but a small quantity was detected. No formation of phenose, $C_6H_6(OH)_6$ (Renard, Abstr., 1881, 721), could be observed.

C. F. B.

Simultaneous Formation of Isomeric Substitution Derivatives of Benzene. By Arnold F. Hollemann (*Rec. Trav. Chim.*, 1900, **19**, 364—376).—The author has studied the composition of the product of the nitration of bromobenzene by the method of solidifying points, as in the case of the nitration of chlorobenzene (Abstr., 1900, i, 638), and by the method of sp. gr. as in the case of the nitration of nitrobenzene (Abstr., 1900, i, 387). In order to prevent the formation of bromodinitrobenzene, the nitric acid used must contain 4 parts of acid of sp. gr. 1·48 to 1 part of acid of sp. gr. 1·52, and the temperature be kept at 0° or at −30° by solid carbon dioxide and alcohol. The method of solidifying points gave, for the composition of the product obtained at 0°, 38·3 per cent. of ortho-, and 61·7 per cent. of parabromonitrobenzene; the method of sp. gr. gave at the same temperature 0·3 per cent. of the meta-, 37·2 per cent. of ortho-, and 62·5 per cent. of para-compound. For the product obtained at −30°, the second method gave 0·3 per cent. of meta-, 34·4 per cent. of ortho-, and 65·3 per cent. of para-bromonitrobenzene.

On comparing these values with those previously obtained (*loc. cit.*), it is seen that the proportion of *o*-nitro-derivative formed is greater with bromobenzene than with chlorobenzene, and that the ratio of the amounts of ortho- and para-compound formed is independent of the temperature. Thus, with similar compounds, such as chloro- and bromo-benzene, the velocity constants of their action with nitric acid is affected by temperature in the same degree. It is noteworthy that the ratio of the quantities of *o*-chloro- and *o*-bromo-benzene corresponding with 100 parts of *p*-chloro- and *p*-bromo-benzene (0·694) is nearly the same as the ratio of the mol. wts. of chloro- and bromo-benzene (0·716).

W. A. D.

Action of Silver Nitrite on Aromatic Halogen-substituted Compounds. By B. ZNATOWICZ (*Bull. Acad. Sci. Cracow*, 1900, 399—400).—The author shows that (1) by the action of silver nitrite on aromatic substances containing halogen in the benzene nucleus, the nitro-group replaces the halogen; (2) iodine is most readily replaced, chlorine least readily; (3) the presence of other groups increases the ease with which the reaction with silver nitrite takes place; (4) oxidation is effected by the silver nitrite at temperatures at which it decomposes. K. J. P. O.

Tervalent Carbon. A Reply. By MAX GOMBERG (*Amer. Chem. J.*, 1901, **25**, 317—335. Compare Norris, this vol., i, 198).—According to the author, hydrogen is not evolved when zinc acts on triphenylchloromethane in perfectly dry ethyl acetate or ether. The unsaturated hydrocarbon is formed in the absence of air, and may be obtained in a practically pure form as large, pale-yellow crystals, but if air is admitted the insoluble peroxide is deposited. The evolution of hydrogen observed by Norris is due to the presence of alcohol and water in his ethyl acetate, as when these compounds are present part of the triphenylchloromethane is hydrolysed or etherified and the hydrogen chloride thus produced acts on the zinc. The yield of peroxide is always much less when moist solvents are employed.

Solutions of hydrogen chloride in dry benzene in contact with zinc evolve hydrogen, although the electrical conductivities of such solutions are practically *nil*.

The fact that the addition of benzene to a mixture of ether and sodium retards the evolution of hydrogen is due, according to the author, to the formation of a slimy protective layer round the sodium.

Various experiments are described which go to prove that (*a*) metals do not cause the evolution of hydrogen chloride from triphenylchloromethane; (*b*) dry air converts the unsaturated hydrocarbon into its peroxide (compare Norris, *loc. cit.*); (*c*) the unsaturated compound is probably colourless. J. J. S.

Phosphates of Aromatic Amines and the Dependence of their Formation and Stability on their Composition and Structure. By P. N. RAIKOW and P. SCHTARBANOW (*Chem. Zeit.*, 1901, **25**, 219—222, 243—245, 261—262, 279—281).—In order to elucidate the influence of the nature and position of substituting groups, the reaction of a number of aromatic amines with phosphoric acid was studied, the amine being warmed with acid of sp. gr. 1·7; the stability of the phosphate formed was also investigated, the salt being subjected to treatment with water, alcohol, and ether. The following regularities were observed: (1) In the presence of foreign solvents (water, alcohol, ether) none of the aromatic bases examined forms a triphosphate. (2) Only aniline and benzylamine form triphosphates when the base is present in excess. (3) When the acid is present in excess, all bases that react with phosphoric acid at all form monophosphates, except *m*- and *p*-aminobenzenesulphonic acids, which form triphosphates; they are the only derivatives of aniline that form triphosphates. (4) With these two exceptions, the derivatives of aniline do not form triphosphates, even when excess of the base is present, but only di- or mono-phosphates or none at all. (5) The substitution of any group in aniline lowers the power of combining with phosphoric acid and the stability of the compound formed. (6) The chemical nature of the substituting group exerts an influence. (7) So does its combining weight, the group of greater weight often exerting the greater influence. (8) So does its position, the influence being greatest in the ortho-, least in the para-position. (9) Water, alcohol, and ether eliminate the base from these phosphates, either wholly, or partially with formation of more acid phosphates. *m*-Phenylenediamine diphosphate, however, is not altered by boiling with water, and β-naphthylamine monophosphate is converted into a diphosphate. (10) Bases with nitrogen in a ring, such as pyrroline, piperidine, quinoline, and *iso*quinoline, only form monophosphates. (11) A benzene ring in the ortho-position exerts the same influence as other substituents; in the meta- and para-positions, on the other hand, it increases the power of combination with phosphoric acid, and this indifferently whether it is attached directly to the main ring as in β-naphthylamine, or quite indirectly as in benzidine and aminoazobenzene.

The phosphates of the aromatic amines are very stable in air and light; apparently they are the form in which the amines are best preserved permanently. The differences which the amines exhibit in their power of combining with phosphoric acid may be utilised in order to separate them in many cases. The phosphates prepared, not always for the first time, are those of the following bases. *Aniline, mono-, di-* (the most stable; melts at 180°), and *tri-phosphates.* o-, m-, and p-*Toluidines,* each *mono* and *di.* 1 : 3 : 5-*Xylidine, mono* and *di*; 1 : 3 : 6, *mono* only. *ψ-Cumidine, mono. Chloroanilines,* o- and m-, *mono* and *di*; p, *mono* (if no *di,* only because the amine is solid and the excess of it could not be separated from the salt). *Bromoanilines,* o, *mono* only; m, *mono* and *di*; p, *mono. Di-* and *tri-bromoaniline,* none. 3 : 5-*Dibromo-*2 : 4-*xylidine, mono.* p-*Iodoaniline, mono.* o- and p-*Hydroxyaniline, mono* (a crystalline meta-salt could not be obtained). o-*Aminothiophenol, mono.* o-*Anisidine, mono.* p-*Phenetidine, mono* and *di. Nitroanilines,* o, none; m and p, *mono. Nitrotoluidines,* $NH_2 : NO_2 : CH_3 =$ 1 : 2 : 4, 1 : 3 : 4, 1 : 3 : 6, and 1 : 2 : 4, *mono. Picramic acid* and *trinitroaniline,* none. *Aminobenzoïc acids,* o, m, and p, *mono. Aminobenzenesulphonic acids,* m and p, *tri.* m-*Phenylenediamine phosphate,* $C_6H_4(NH_2)_2,2H_3PO_4$. p-*Phenylenediamine* and *diaminotetrahydroxybenzene,* none. *Benzylamine, mono, di,* and *tri. Phenylhydrazine, mono* and *di. Tolylhydrazines,* o- and p-, *mono. Acetyl-* and *benzoyl-phenylhydrazine,* none. *Aminoazobenzene, mono. Pyrrole, mono. Piperidine, mono. Benzidine phosphates,* $C_{12}H_8(NH_2)_2,2H_3PO_4$ and

$$C_{12}H_8(NH_2)_2,H_3PO_4.$$

Naphthylamines, α, *mono*; β, *mono* and *di. Quinoline, mono.* iso*Quinoline, mono.*

C. F. B.

New Synthesis of Aniline. By George F. Jaubert (*Compt. rend.,* 1901, **132**, 841—842).—Aniline or *p*-toluidine may be synthesised from benzene or toluene, and obtained in the form of hydrochloride by heating together hydroxylamine hydrochloride and the corresponding hydrocarbon in the presence of aluminium or zinc chloride; the yield obtained by this method is not, however, very good. G. T. M.

Halogen-substituted Aminomercaptans. By ALEXANDER EIBNER (*Ber.*, 1901, **34**, 657—660).—When trichloroethylidenedianiline, $CCl_3\cdot CH(NHPh)_2$, is mixed with thioacetic acid, hydrogen sulphide is evolved, and acetanilide and *acetylphenyl-α-aminotrichloroethylhydrosulphide*, $CCl_3\cdot CH(SH)\cdot NAcPh$, are obtained. The latter substance melts at 99°; it appears to be the first instance met with of an α-aminohydrosulphide, that is one in which the amino-group and sulphur atom are attached to the same carbon atom; it is not a very stable substance; dilute acids readily decompose it into chloral, hydrogen sulphide, and acetanilide.

When benzylideneaniline, $NPh{:}CHPh$, is dissolved in a mixture of light petroleum and ether, and thioacetic acid is added, a *substance*, $NAcPh\cdot CHPh\cdot SH$, melting at 75°, is obtained; this is unstable, decomposing readily into acetanilide and thiobenzaldehyde.

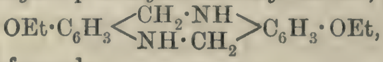
Thioacetic acid does not react readily with phenylthiocarbimide; at 200°, acetanilide and carbon disulphide are, however, formed. Addition probably takes place as an intermediate stage. C. F. B.

Nitro-derivatives of *o*-Anisidine. By GEORGES FREYSS (*Bull. Soc. Ind. Mulh.*, 1900, **70**, 375—383).—By the action of nitric acid on acetyl-*o*-anisidine, two mononitro-derivatives are produced. p-*Nitro-o-acetylanisidine*, $NO_2\cdot C_6H_3(OMe)\cdot NH_2$, $[OMe : NH_2 : NO_2 = 1 : 2 : 5]$, melts at 153—154°, and is hydrolysed to p-*nitro-o-anisidine* melting at 139—140°; by replacing the amino-group with hydrogen, the latter compound is converted into *m*-nitroanisole; the constitution of the nitroanisidine was established by reducing it to the *p*-diamine melting at 220°, and by converting it by means of alkali hydroxide into *p*-nitroguaiacol, $NO_2\cdot C_6H_3(OMe)\cdot OH$ $[OMe : OH : NO_2 : 1 : 2 : 5]$. The *ethyl* ether of *p*-nitroguaiacol melts at 85—86°, and is converted by reduction and acetylation into a *methoxyphenacetin*, $OEt\cdot C_6H_3(OMe)\cdot NHAc$, $[OMe : OEt : NHAc = 1 : 2 : 5]$.

m-Nitro-*o*-anisidine, $NO_2\cdot C_6H_3(NH_2)\cdot OMe$ $[OMe : NH_2 : NO_2 = 1 : 2 : 4]$, melts at 116·5—117·5°, is identical with the nitroanisidine produced by the reduction of dinitroanisole (Cahours, *Annalen*, 1850, **74**, 301), and is converted by elimination of the amino-group into *p*-nitroanisole, thus establishing its constitution. The *acetyl* derivative melts at 175—176°; it is produced by the action of nitric acid on acetyl-*o*-anisidine, and is the sole product of the action when the nitration is carried out in sulphuric acid solution with 1 mol. of nitric acid.

The two nitroacetylanisidines described above are converted by further nitration into Meldola and Wechsler's dinitroacetaniside (Trans., 1900, **77**, 1172), thus establishing the position of the nitro-groups in the latter. Attempts to eliminate the amino-group from dinitro-*o*-anisidine gave the monomethyl ether of *o*-nitroresorcinol $[OMe : OH : NO_2 = 1 : 3 : 4]$, one of the nitro-groups being replaced by hydroxyl; the *dimethyl* ether, $C_6H_3(OMe)_2\cdot NO_2$, $[(OMe)_2 : NO_2 = 1 : 3 : 4]$, melts at 72—73°, and is reduced to aminodimethylresorcinol (Bechhold, Abstr., 1889, 1155). T. M. L.

Action of Formaldehyde on *p*-Formylphenetidine. By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1901, **25**, 178. Compare Abstr., 1900, i, 285, 436).—*p*-Formylphenetidine is decomposed by strong hydrochloric acid in the cold. It dissolves in excess of formaldehyde; from the solution, water precipitates an oil which decomposes spontaneously into formaldehyde and *p*-formylphenetidine. If the solution is allowed to remain in the cold with a very little dilute hydrochloric acid, however, crystalline *anhydro-*p*-ethoxyaminobenzyl alcohol*,



$$\mathrm{OEt\cdot C_6H_3}<\substack{\mathrm{CH_2\cdot NH} \\ \mathrm{NH\cdot CH_2}}>\mathrm{C_6H_3\cdot OEt},$$

melting at 140°, is formed.

Valerylaniline and valeryl-*p*-phenetidine yield amorphous *p*-anhydrovalerylaminobenzyl and anhydrovalerylethoxyaminobenzyl alcohols respectively when heated with excess of formaldehyde and strong hydrochloric acid. C. F. B.

Reactions of Nitroxyl [NOH]. By ANGELO ANGELI and FRANCESCO ANGELICO (*Atti Real. Accad. Lincei*, 1901, [v], **10**, i, 164—168. Compare Abstr., 1900, ii, 594).—Salts of nitrohydroxylaminic acid are readily resolved into the corresponding nitrites and the unsaturated residue nitroxyl, $\vdots\mathrm{N\cdot OH}$, which, in presence of aldehydes, nitroso-derivatives, amines, &c., yields additive products. This reaction has been further studied, the results being as follows.

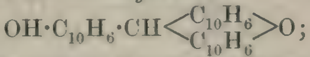
Benzaldehyde, anisaldehyde, piperonylaldehyde, acetaldehyde, and formaldehyde react with salts of nitrohydroxylaminic acid, yielding the corresponding substituted hydroxamic acids.

With nitrosobenzene and nitroso-*p*-toluene, salts of nitrohydroxylaminic acid give the nitroso-derivatives of phenylhydroxylamine and *p*-tolylhydroxylamine respectively.

The additive compounds formed by the action of nitrohydroxylaminates with aliphatic secondary amines (piperidine and coniine) give up water, the residues of 2 mols. then uniting to form tetrazones.

T. H. P.

Iodo-derivatives of Phenol. By P. BRENANS (*Compt. rend.*, 1901, **132**, 831—833).—A mixture of 2 : 4-diiodophenol and 2 : 4 : 6-triiodophenol is obtained on adding a potassium hydroxide solution of phenol, containing excess of the alkali, to a potassium iodide solution of iodine; the quantities of these derivatives produced depend on the relative proportions of phenol and iodine employed in the experiment; when the latter substance is in considerable excess and the solution is rendered strongly alkaline, diiodophenol iodide is precipitated as a violet-red, amorphous compound. The acetyl derivative of 2 : 4-diiodophenol melts at 70—71°, not at 76° as stated by Neuman and Vater (*Annalen*, 1887, **241**, 81). G. T. M.

The Supposed Dinaphthylene Alcohol. By R. FOSSE (*Compt. rend.*, 1901, **132**, 695—697. Compare Rousseau, Abstr., 1882, 735, 1211, 1299).—On applying Tiemann and Riemer's reaction to β-naphthol, Rousseau obtained, together with other products, a substance which decomposed at 260°, and was supposed by him to be dinaphthylene alcohol, $C_{22}H_{14}O$. The author shows that this compound has, in reality, the empirical formula $C_{31}H_{20}O_2$, and is the eso*anhydride* of 2 : 2′ : 2″-*trihydroxy*-1 : 1′ : 1″-*trinaphthylmethane*,  $OH\cdot C_{10}H_6\cdot CH<\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}>O$; it is produced by the action of chloroform on sodium β-naphthoxide in sealed tubes at 150°, and may also be prepared synthetically from 2-hydroxy-1-naphthaldehyde and β-naphthol by condensation in acetic acid solution in the presence of sulphuric acid. The compound is obtained pure by repeated crystallisation, first from nitrobenzene, and then from acetone; when separating from the latter medium, the crystals contain a certain amount of the solvent, and when freed from this, melt at 273° to a brown liquid; it is insoluble in aqueous alkalis, but dissolves in their alcoholic solutions. The *acetyl* derivative of the preceding compound melts at 285°. G. T. M.

Naphthylol-naphthyl-oxynaphthylmethane. By R. Fosse (*Compt. rend.*, 1901, **132**, 787—789).—A more detailed account of *naphthylol-naphthyl-oxynaphthylmethane* [*eso*anhydride of 2 : 2′ : 2″-trihydroxy-1 : 1′ : 1″-trinaphthylmethane] (preceding abstract). Its *methyl* ether melts at 255°, and its *ethyl* ether at 304°. Cryometric determinations with the former show that its molecular weight is 438.

C. H. B.

Acidimetric Value of Monosubstituted Benzoic Acids. By Gustave Massol (*Compt. rend.*, 1901, **132**, 780—781).—The author has determined the heat of formation, from solid acid and solid alkali hydroxide, of the solid anhydrous salts of the monosubstituted derivatives of benzoic acid.

	Ortho.	Meta.	Para.
Sodium hydroxybenzoate ...	+19·15 Cal.	+17·77 Cal.	+17·79 Cal.
„ bromobenzoate	+17·99 „		+17·39 „
„ chlorobenzoate	+18·87 „		
„ iodobenzoate	+17·73 „		
„ nitrobenzoate	+20·36 „	+19·39 „	+19·31 „

The heat of formation of sodium benzoate is +17·40 Cal., and the somewhat varying effect of the substitutions is readily recognised. In the ortho-derivatives, the nitro-group has the greatest effect, and the hydroxyl group comes next. In the meta- and para-derivatives the nitro-group has a relatively large effect, whilst the hydroxyl group has very little effect. C. H. B.

Thermochemistry of *o*-Chloro- and *o*-Iodo-benzoic Acids. By Gustave Massol (*Bull. Soc. Chim.*, 1901, [iii], **25**, 195—196. See this vol., ii, 226).

Thermochemistry of *o*- and *p*-Bromobenzoic Acids. By Gustave Massol (*Bull. Soc. Chim.*, 1901, [iii], **25**, 369—371).—The solubility of *o*-bromobenzoic acid in water is too small to allow of its heat of dissolution being determined. The sodium salt becomes anhydrous at 110°, and dissolves in water with the development of 3·08 Cal. From the heat of neutralisation,

$$C_6H_4Br\cdot CO_2H\ (sol.) + NaOH\ (diss.) = C_6H_4Br\cdot CO_2Na\ (diss.) + 9{\cdot}86\ Cal.$$

the heat of formation of the anhydrous sodium salt from the solid base and acid is calculated to be 17·99 Cal.

The heat of dissolution of *p*-bromobenzoic acid also could not be determined. The sodium salt becomes anhydrous at 100°; its heat of dissolution is − 0·38 Cal. From the heat of neutralisation,

$C_6H_4Br{\cdot}CO_2H$ (sol.) + NaOH (diss.) = $C_6H_4Br{\cdot}CO_2Na$ (diss.) + 5·80 Cal.,

the heat of formation of the anhydrous salt is calculated to be 17·39 Cal., all the substances concerned being in the solid state. This result is almost identical with the corresponding value (17·4 Cal.) for sodium benzoate. The progressively decreasing influence of substituted chlorine, bromine, and iodine is well shown in the heats of formation of sodium benzoate (17·4 Cal.), *o*-chlorobenzoate (18·87 Cal.), *o*-bromobenzoate (17·99 Cal.), and *o*-iodobenzoate (17·73 Cal.).

N. L.

Conversion of Anethole into Anisic Acid by Five successive Oxidations. By J. BOUGAULT (*Compt. rend.*, 1901, **132**, 782—784).—Methoxyhydratropic acid, obtained (Abstr., 1900, i, 495) by the action of silver oxide on the aldehyde prepared by oxidising anethole with mercuric oxide and iodine, is in its turn oxidised by chromic mixture and converted into *p*-methoxyacetophenone. This ketone, when oxidised by potassium permanganate in alkaline solution, yields *p*-methoxyphenylglyoxylic acid. This is converted into anisic acid by the action of permanganate in acid solution. C. H. B.

Metallic "Saccharinates." By H. DEFOURNEL (*Bull. Soc. Chim.*, 1901, [iii], **25**, 322—329).—Only the sodium, potassium, barium, and silver derivatives of "saccharin" (*o*-benzoicsulphinide) seem to have hitherto been described. The *lithium, copper, calcium, strontium, magnesium, zinc, mercury, cadmium, lead, manganese, cobalt, iron,* and *nickel* salts have therefore been prepared and analysed, and are described in the paper; they are obtained either by the action of "saccharin" on the metallic carbonates or by double decomposition from the sodium derivative and the metallic sulphates. N. L.

A Simple Synthesis of δ-Ketonic Acids. By HANS STOBBE [and in part HANS VOLLAND] (*Ber.*, 1901, **34**, 653—656).—When a mixture of acetophenone and ethyl cinnamate is added gradually to a suspension of sodium ethoxide in ether, cooled in a freezing mixture, and the whole is allowed to remain at first in the freezing mixture, afterwards at the ordinary temperature, partial condensation takes place with formation of γ-benzoyl-β-phenylbutyric acid,

$$CPhO{\cdot}CH_2{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H,$$

(Vorländer and Knötzsch, Abstr., 1897, 286); this can be separated from uncondensed cinnamic acid by means of its *semicarbazone*, which is but little soluble in dilute alcohol, and melts at 212·5—213°.

C. F. B.

New Derivatives of Dimethylaminobenzoylbenzoic Acid. By ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1901, **132**, 746—750. Compare Abstr., 1900, i, 170; this vol., i, 146, 276).—*Nitrodimethylaminobenzoylbenzoic acid* forms small, yellow prisms containing $1H_2O$, which is lost at about 100°, the anhydrous acid melting at 170°. When heated with sulphuric acid and mercuric sulphate, it yields phthalic acid. Methyl dimethylaminobenzoylbenzoic acid forms yellow prisms insoluble in water and only slightly soluble in cold organic solvents, but soluble in the latter on heating. It melts at 140°, and not 163° as stated by Limpricht (*Annalen*, 1899, **307**, 307), whose product was probably *p*-nitrodimethylaniline *Nitrodimethylanilinephthalein*, obtained by the condensation of dimethylaniline with nitrodimethylaminobenzoylbenzoic acid in presence of acetic acid, crystallises from a mixture of alcohol and chloroform in orange prisms melting at 175°; it forms salts which are readily decomposed by water. When reduced, it yields *aminodimethylanilinephthalein* in white needles melting at 179°; its *acetyl* derivative forms colourless prisms which melt at 157°. An isomeride of the latter, crystallising in colourless prisms which melt at 209° and are much more soluble in alcohol, is obtained by condensing dimethylaminobenzoylbenzoic acid with *m*-aminodimethylaniline in presence of acetic anhydride.

In the nitrodimethylaminobenzoylbenzoic acid, the nitro-group is most probably in the ortho-position with respect to the dimethylamino-group.
C. H. B.

isoAlantolactone, a Bye-product in the Preparation of Alantolactone. By JULIUS SPRINZ (*Ber.*, 1901, **34**, 775—781).—iso*Alantolactone*, described by Dumas (*Arch. de Pharm.*, 1835, **15**, 158) as 'helenin,' and regarded by Kallen as having the composition $(C_6H_8O)_n$ (Abstr., 1874, 352) melts at 115°, has the empirical formula $C_{15}H_{20}O_2$, and a corresponding molecular weight, as determined from the freezing point of a solution in benzene. By warming with sodium hydroxide, it is hydrolysed to iso*alantolic acid*, $OH\cdot C_{14}H_{20}\cdot CO_2H$, of which the *silver*, *barium*, and *calcium* salts are also described. The *ethyl* ester separates from absolute alcohol in colourless, rhombic crystals. The *amide* crystallises from alcohol in white needles and melts at 237—239°; its *acetyl* derivative, $C_{17}H_{25}O_3N$, crystallises from acetic acid and melts at 212°.

*Dihydro*iso*alantolactone*, $C_{15}H_{22}O_2$, prepared by the action of sodium amalgam on the lactone, melts at 166°. The *acid*, $C_{15}H_{24}O_3$, melts at 122—123°. The *amide*, $C_{15}H_{25}O_2N$, forms prismatic needles and melts at 176°.

iso*Alantolactone monohydrochloride*, $C_{15}H_{20}O_2,HCl$, crystallises from hot alcohol in colourless needles and melts at 153°. The *dihydrochloride*, $C_{15}H_{20}O_2,2HCl$, was obtained as a syrupy liquid.

*iso*Alantolactone yields a nitro-derivative, and when distilled with zinc dust appears to give traces of naphthalene; it has not been converted into alantolactone.
T. M. L.

Esterification of 3-Nitrophthalic Acid. By RUDOLF WEGSCHEIDER (*Ber.*, 1901, **34**, 680—681. Compare this vol., i, 32).—In reply to Marckwald and McKenzie (this vol., ii, 229), the author points out that he had previously observed the formation of normal ester but not of the isomeric acid ester as the amount of acid employed was small.
J. J. S.

Peracids and Peroxide Acids derived from Dibasic Organic Acids. By ADOLF BAEYER and VICTOR VILLIGER (*Ber.*, 1901, **34**, 762—767. Compare Pechmann and Vanino, Abstr., 1894, i, 416. Thiele, Abstr., 1896, i, 597).—*Monoperphthalic acid*, $CO_2H\cdot C_6H_4\cdot CO_3H$, prepared by shaking together finely divided phthalic anhydride and an alkaline solution of hydrogen peroxide until the former passes into solution, is extracted by ether from the acidified solution and crystallises from this solvent in needles decomposing at 110°. The compound resembles perbenzoic acid, liberating iodine from hydriodic acid and oxidising aniline to nitrosobenzene; it may also be obtained by hydrolysing phthalic peroxide with cold sodium hydroxide solution.

Phthalic acid peroxide, $O_2(CO\cdot C_6H_4\cdot CO_2H)_2$, is produced either by treating the alkaline solution of the preceding compound with phthalic anhydride or by the direct action of hydrogen peroxide solution on finely divided phthalic anhydride in the presence of sodium hydroxide, a larger proportion of the anhydride being employed than in the preceding experiment. The compound is slightly soluble in the ordinary solvents; it crystallises in small needles from its concentrated solution in sodium hydrogen carbonate. The *ethyl* ester of the preceding compound is obtained by the oxidation of Zelinsky's ethylphthalic chloride (Abstr., 1887, 669) with an alkaline solution of hydrogen peroxide. The compound crystallises from methyl alcohol in leaflets and melts at 58—59°; it is easily soluble in the ordinary solvents with the exception of water and petroleum. A cryoscopic determination of the molecular weight gives numbers agreeing with the double formula $O_2(CO\cdot C_6H_4\cdot CO_2Et)_2$.

Diperterephthalic acid, $C_6H_4(CO_3H)_2$, produced by shaking together an ethereal solution of terephthalic chloride and an alkaline solution of hydrogen peroxide, is isolated in the form of its sparingly soluble *monosodium* salt by saturating the product of reaction with carbon dioxide. The salt crystallises in hexagonal plates and explodes on heating or on percussion; it has a neutral reaction and dissolves in sodium hydroxide solution with the formation of a disodium salt. It furnishes white, crystalline precipitates with calcium and barium chlorides, white, amorphous deposits with lead and zinc sulphates, and a light blue, insoluble powder with copper sulphate. The *acid* is obtained in slender, felted needles by acidifying a solution of the disodium salt with dilute sulphuric acid; it is very sparingly soluble, 1 gram requiring 18 litres of cold water; it explodes when heated or on percussion. It is readily converted into terephthalic acid by reducing agents; with manganous salts, it yields a precipitate of the dioxide, whilst aniline is oxidised to nitrosobenzene. G. T. M.

Derivatives of Gallamic Acid. By ROBERT GNEHM and AUG. W. E. GANSSER (*J. pr. Chem.*, 1901, [ii], **63**, 77—93).—Gallamide reacts with aminophenyl ethers at 180—200° according to the equation

$$C_6H_2(OH)_3\cdot CO\cdot NH_2 + NH_2\cdot C_6H_4\cdot OR = C_6H_2(OH)_3\cdot CO\cdot NH\cdot C_6H_4\cdot OR + NH_3.$$

The resulting gallaminophenyl ethers are easily decomposed by alkalis, but are fairly stable in the presence of mineral acids. *Gallamino-p-phenyl methyl ether* melts at 214°, and the *ethyl* ether at 219°;

gallamino-o-phenyl methyl ether melts at 238—239°. Gallamide also reacts similarly with aminonaphthyl ethers, but the resulting products are not described.

Gallamide reacts with α- and β-naphthylamines at 180—210° in the same way as with aniline; *α-gallonaphthylamine* crystallises in white needles and melts at 136°. Experiments with *p*-phenylenediamine hydrochloride or benzidine gave crystalline products, which were not further investigated.

Gallamide is very readily brominated in chloroform solution, with the formation of mono- or di-bromogallamide, according to the quantity of halogen employed. Crystals of these substances deposited from aqueous solution contain water of crystallisation. *Bromogallamide*, $C_6HBr(OH)_3\cdot CO\cdot NH_2,1\frac{1}{2}H_2O$, melted at 194—195°, but when anhydrous at 204—205°; *dibromogallamide*, $C_6Br_2(OH)_3\cdot CO\cdot NH_2,3\frac{1}{2}H_2O$, melted at 241—243°, but when anhydrous at 245°. Both these substances gave an intense blue colour with ferric chloride, and also with alkalis, although in the latter case the colour changed to red on warming; they were completely decomposed by strong sulphuric acid, but were not altered when boiled with dilute acids.

Gallaminophenyl ethers yield tribromo-derivatives with bromine in chloroform solution. *Tribromogallamino-*p*-phenetole*,

$$C_6Br_2(OH)_3\cdot CO\cdot NH\cdot C_6H_3Br\cdot OEt,$$

melts at 218—219°, gives a yellowish-green coloration with ferric chloride (soon succeeded, however, by a flocculent precipitate), and is decomposed in the cold by potassium hydroxide.

Gallaminophenyl ethers, when boiled with acetic anhydride, yield triacetyl derivatives; *triacetylgallamino-*p*-phenetole*,

$$C_6H_2(OAc)_3\cdot CO\cdot NH\cdot C_6H_4\cdot OEt,$$

crystallises from alcohol or toluene in needles, melts at 133—134°, and gives no coloration with ferric chloride. On similarly treating mono- or di-bromogallamide, four acetyl groups are introduced; *tetra-acetylbromogallamide*, $C_6HBr(OAc)_3\cdot CO\cdot NHAc$, melts at 240°, and *tetra-acetyldibromogallamide* at 233°.

Gallamide, gallanilide, and gallaminophenyl ethers react with formaldehyde in presence of hydrogen chloride, in much the same way as does gallic acid itself (compare Möhlau and Kahl, Abstr., 1898, i, 260), forming methylenedigallamides.

A substituted gallamine-blue is obtained by the interaction of gallamino-*p*-phenetole and nitrosodimethylaniline hydrochloride. It is sparingly soluble in water or alcohol, gives a deep blue solution with strong sulphuric acid, a reddish-violet solution with dilute sulphuric acid or alkalis, and a magenta solution with strong hydrochloric acid. Red colouring matters are obtained by the interaction of mono- or di-bromogallamide with nitrosodimethylaniline hydrochloride.

W. A. B.

Synthesis of Aromatic Aldehydes. By ALEXANDR REFORMATSKY (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 154—157).—By passing a mixture of hydrogen chloride and carbon monoxide through benzene containing freshly prepared aluminium bromide and cuprous chloride in solution, about 85—90 per cent. of the theoretical yield of benzaldehyde is obtained. The mechanism of the reaction is thus explained. Hydrogen chloride and aluminium bromide give aluminium chloride and hydrogen bromide, the latter, in the nascent state and in presence of cuprous chloride, then condensing with the carbon monoxide to form the bromoanhydride of formic acid. This bromoanhydride, which readily loses bromine, reacts with benzene, yielding hydrogen bromide and benzaldehyde. T. H. P.

Hydroxynaphthaldehyde or 1-Methanal-2-naphthylol. By R. Fosse (*Bull. Soc. Chim.*, 1901, [iii], **25**, 371—375).—The processes employed by Rousseau and by Kauffmann for the isolation of hydroxynaphthaldehyde from the products of the action of chloroform and sodium hydroxide on β-naphthol are very tedious and unsatisfactory. By working in dilute alcoholic solution, with the precautions described in detail in the paper, the formation of bye-products is reduced to a minimum, and more than 86 per cent. of the theoretical yield of the aldehyde is obtained. Hydroxynaphthaldehyde crystallises from alcohol in prisms and from acetic acid in needles, melts at 77°, and boils at 192° under 27 mm. pressure. The *oxime* crystallises in long, silky needles melting at 157°, and the *phenylhydrazone* forms crystals melting at 195°. With aniline, *o*-toluidine, and *p*-toluidine, hydroxynaphthaldehyde forms yellow, crystalline *hydramides* melting at 87°, 124°, and 132° respectively; the compound with α-naphthylamine crystallises in magnificent, coral-red needles melting at 180°. N. L.

Oxidation of Mesityl Methyl Ketone and the Preparation of Trimethylbenzoic Acid. By L. van Scherpenzeel (*Rec. Trav. Chim.*, 1900, **19**, 377—385).—Claus' method (Abstr., 1890, 981) of oxidising mesityl methyl ketone with 0·4 per cent. aqueous potassium permanganate gives only a poor yield of mesitylglyoxylic acid, but by using a slightly alkaline 3 per cent. solution at 0° (compare Dittrich and Meyer, Abstr., 1891, 1224) good results are obtained; the mesitylglyoxylic acid is best isolated by acidifying with sulphuric acid and extracting with benzene. From the acid solution remaining, mesitylglycollic acid, $C_6H_2Me_3\cdot CH(OH)\cdot CO_2H$ (m. p. 151—152°; Feith, Abstr., 1892, 329, gives 147°; methyl ester, m.p. 90—91°, Feith gives 92°), can be isolated, its formation being probably due to the action of the alkali, present during the oxidation, on the *aldehyde*, $C_6H_2Me_3\cdot CO\cdot CHO$, initially formed, a case similar to the transformation by alkalis of glyoxal into glycollic acid. Mesitylglycollic acid is characterised by dissolving in concentrated sulphuric acid with an increasingly red coloration.

The statements of Claus (*loc. cit.*) and of Nass (*Diss. Freiburg*, 1889) concerning the preparation of trimethylbenzoic acid seem to be incorrect; with slightly alkaline 0·75 per cent. aqueous potassium permanganate at the ordinary temperature, mesityl methyl ketone yields principally mesitylglyoxylic acid, which, when separated and left in contact with an amount of the oxidising solution sufficient to form trimethylbenzoic acid, is not further changed beyond yielding a small quantity of an *acid*, $C_{11}H_{10}O_5$ crystallising from water and melting and decomposing at 220—222°. This acid fails to yield crystalline salts, and is not apparently the acid $CO_2H\cdot C_6H_2Me_2\cdot CO\cdot CO_2H$, as it is not changed either by alkaline potassium permanganate at 60° or by warm nitric acid of sp. gr. 1·1. Mesitylglyoxylic acid is not oxidised by warming with an ammoniacal solution of silver nitrate, but when boiled with dilute nitric acid of sp. gr. 1·1 for several hours, it yields about 24 per cent. of its weight of trimethylbenzoic acid, the principal product being an acid which "may be a dimethylphthalic acid, but is certainly not" the foregoing acid melting at 220—222°. Trimethylbenzoic acid is best prepared by warming mesitylglyoxylic acid with concentrated sulphuric acid. W. A. D.

Action of Mercaptan on Quinones. By TARBOURIECH (*Bull. Soc. Chim.*, 1901, [iii], **25**, 313—315).—The action of ethyl mercaptan on quinone results in the formation of quinol and quinhydrone, the mercaptan being reduced to thioaldehyde, C_2H_4S, but under certain conditions a *compound* crystallising in large, red needles is obtained, which is formed by the substitution of two SEt groups for two hydrogen atoms in the quinone nucleus. Ethyl mercaptan has no action on anthraquinone or phenanthraquinone, a result which confirms Posner's observation (this vol., i, 14) that only those diketones yield mercaptoles which contain carbonyl groups attached to methyl radicles.

N. L.

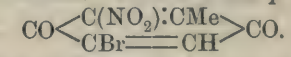
Chemical Action of Light. By GIACOMO L. CIAMICIAN and PAUL G. SILBER (*Atti Real. Accad. Lincei,* 1901, [v], **10**, i, 92—103). —Under the influence of light, quinone and alcohol react, yielding, as was shown by Ciamician (Abstr., 1886, 695), quinol and acetaldehyde. The study of this action of light has now been extended, the following being the results obtained.

*iso*Propyl alcohol and quinone give acetone and quinone, whilst *tert.*butyl alcohol and quinone yield quinol and quinhydrone. Glycerol and quinone give rise to quinhydrone and glycerose, the latter yielding an osazone melting at 136—137°, and not at 131° as stated by Fischer and Tafel (Abstr., 1887, 651). Erythritol and quinone form quinhydrone and erythrose, whilst from *d*-mannitol and quinone are obtained quinhydrone and *d*-mannose. Dulcitol and quinone give a sugar which, with phenylhydrazine, yields the dulcosazone of Fischer and Tafel (Abstr., 1888, 358). In the case of dextrose and quinone, the products are quinhydrone and glucosone.

Thymoquinone and alcohol give acetaldehyde and thymoquinol, the latter melting at 143°, whilst Carstanjen (this Journal, 1871, 351) gave 139·5°. With phenanthraquinone and mannitol, only very slight action takes place.

Quinone has no definite action on lactic, malic, or tartaric acid beyond the evolution of carbon dioxide. With acetic or propionic acid, quinone produces only a gradual darkening, whilst with formic acid it gives quinol and carbon dioxide. The reduction of quinone by benzene is slow, but with the paraffins the action is very rapid and yields products not yet investigated.

The sole products of the reaction between benzophenone and alcohol are acetaldehyde and benzopinacone. For the last-named compound, obtained by the reduction of benzophenone by means of zinc and acetic acid, Zagumenny (Abstr., 1881, 813) gave the melting point 168°; the authors' product melts at 185—187°, and that prepared by Zagumenny's method at 186°. Acetophenone is completely converted by the action of alcohol into acetophenonepinacone and *iso*acetophenonepinacone. Benzaldehyde and alcohol yield hydrobenzoin, *iso*hydrobenzoin, and a resinous polymeride which, when precipitated from benzene solution by the addition of light petroleum, softens at 100—101° and has probably the composition $(C_{14}H_{14}O_4)_4$. The action of alcohol on anisaldehyde is slow and gives a small yield of hydroanisoin. Benzoin is oxidised by alcohol with the formation of hydrobenzoin, *iso*hydrobenzoin, and a large proportion of resinous matter, consisting to a small extent of benzoic acid. An alcoholic, ethereal, or acetone solution of vanillin, on exposure to light, gradually deposits crystals of dehydrovanillin. T. H. P.

Action of Nitric Acid on Halogen Derivatives of *p*-Cresol. By Theodor Zincke (*J. pr. Chem.*, 1901, [ii], 63, 183—187. Compare Abstr., 1900, i, 545).—The action of nitric acid on the halogen derivatives of *p*-cresol is shown not to yield oxyketones [ψ-quinols] as stated in the previous paper (*loc. cit.*), but toluquinone derivatives. A wandering of the methyl group to the neighbouring carbon atom has thus taken place in the reaction. Thus 3-bromo-*p*-cresol yields 4 : 2-bromonitro-*p*-toluquinone,  $CO<\begin{matrix}C(NO_2){:}CMe\\ CBr{=\!=\!=}CH\end{matrix}>CO$. Probably oxyketones [$\psi$-quinols] are intermediate products (compare Bamberger, this vol., i, 140), but they have not been isolated.

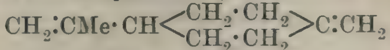
2 : 4- (or 4 : 2-) *Chloronitro*-p-*toluquinone* forms bright yellow, flattened needles melting and decomposing at 128°. By reduction with tin and hydrochloric acid, *chloroamino*-p-*toluquinol* is obtained, crystallising in slender needles which melt and decompose at 160—162°, and readily oxidise. The *triacetyl* derivative forms long, slender needles melting at 198°.

2 : 4- (or 4 : 2-) *Bromonitro*-p-*toluquinone* resembles the chloro-derivative, and melts and decomposes at 135—136°. *Bromonitro*-p-*toluquinol* is obtained from the nitro-compound by reduction with hydriodic acid, and forms long, yellow needles melting at 175°. The *diacetyl* derivative forms colourless, lustrous, four-sided prisms melting at 118°. *Bromoamino*-p-*toluquinol* forms needles melting and decomposing at 148—149°. The *triacetyl* derivative forms aggregates of needles melting at 203—204°.

2 : 5 : 4- (or 4 : 5 : 2-) *Dibromonitro*-p-*toluquinone* crystallises in yellow plates or leaflets melting and decomposing at 175—180°. *Dibromonitro*-p-*toluquinol* forms long, silky needles melting at 157—158°, and dissolves in alkali carbonate solutions with a deep red colour.

K. J. P. O.

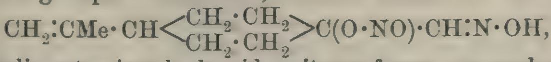
Elimination of Water, Halogen Hydride, and Ammonia in the Terpene Series. By Friedrich W. Semmler (*Ber.*, 1901, 34, 708—719).—The author, after discussing the formation of terpinene from terpin, dihydrocarveol, and dihydrocarvylamine, concludes from the following facts that terpinene is *ψ-limonene*,



$$CH_2{:}CMe\cdot CH{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}{>}C{:}CH_2$$

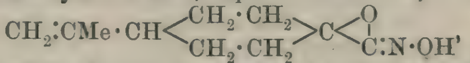
(compare Abstr., 1900, i, 452; and Wallach, *Annalen*, 1893, **277**, 146).

On warming terpinene nitrosite,



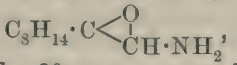
$$CH_2{:}CMe\cdot CH{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}{>}C(O\cdot NO)\cdot CH{:}N\cdot OH,$$

with alcoholic potassium hydroxide, nitrous fumes are evolved, and on pouring immediately into water, *terpineneoxideoxime*,



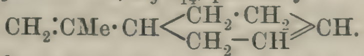
$$CH_2{:}CMe\cdot CH{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}{>}C{<}\begin{matrix}O\\ |\\ C{:}N\cdot OH\end{matrix}$$

separates as a white, flocculent mass which melts at about 85°, decomposes when distilled under diminished pressure, and changes when dried in a vacuum into a liquid *isomeride*, although stable when kept in the air. On reduction with sodium and alcohol, the *base*,



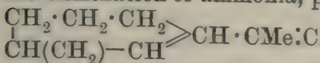
$$C_8H_{14}\cdot C{<}\begin{matrix}O\\ |\\ CH\cdot NH_2\end{matrix}$$

boiling at 140—150° under 20 mm. pressure, is obtained. The direct reduction of terpinene nitrosite, on the contrary, yields, in addition to the compounds described by Wallach (this vol., i, 90), a solid *base* melting at 88°, and a *hydrocarbon*, C_9H_{14}, probably



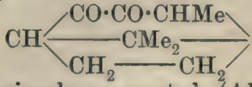
$$CH_2{:}CMe\cdot CH{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2-CH\end{matrix}{>}CH.$$

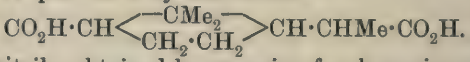
According to the formula given above, terpinene should interact additively with bromine; although, as found by Wallach, this is not the case, its nitrosite combines directly with bromine in glacial acetic acid solution to form, amongst other compounds, a crystalline substance melting at 102°. Von Baeyer found that Beckmann's solution precipitates terpinene (Abstr., 1894, i, 297),, and it is now shown that the former is a characteristic reagent for pseudoterpenes or terpene alcohols, for example, sabinene or sabinol.

Carvestrene, boiling at 180—186°, obtained from vestrylamine by the elimination of ammonia, probably contains a quantity of the *ψ-form*,  $\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\ |\\ CH(CH_2)-CH\end{matrix}{>}CH\cdot CMe{:}CH_2$, as the dihydrobromide, when heated with quinoline, yields the true ortho-carvestrene boiling at 178°.

Sabinene, when treated with nitrous acid, fails to yield a definite compound.

W. A. D.

Terpenes and Ethereal Oils. Studies in the Fenchone Series. By Otto Wallach (*Annalen*, 1901, **315**, 273—303. Compare Abstr., 1900, i, 241).—[With Wilhelm von Westphalen.]—The neutral crystalline *compound* obtained as a bye-product in the preparation of fenchocarboxylic acid from fenchone may be either a pinacone, $C_{20}H_{34}O_2$, or a difenchone, $C_{20}H_{32}O_2$, produced from 2 mols. of the ketone by a condensation similar to that observed in the case of dimethyl*cyclo*hexenone (Knoevenagel, Abstr., 1899, i, 340). The substance does not yield well-defined derivatives, and decomposes when heated under reduced pressure at temperatures below 100° into fenchone and an uncrystallisable product. The compound, $C_{11}H_{16}O_2$, obtained by the dry distillation of lead fenchocarboxylate is in reality an ortho-diketone,  $\mathrm{CH}\left\langle\begin{array}{c}\mathrm{CO\cdot CO\cdot CHMe}\\ \mathrm{CMe_2}\\ \mathrm{CH_2-CH_2}\end{array}\right\rangle\mathrm{CH}$, and not an ortho-hydroxyketone, as previously suggested (Abstr., 1898, i, 487); it is accordingly termed *carbofenchonone* instead of hydroxycarbofenchonone. The *alcohol*, $C_{11}H_{18}O_2$, formed by the action of zinc dust and acetic acid on the diketone, crystallises from dilute alcohol and melts at 89°. Carbofenchone, on oxidation, yields a dicarboxylic *acid*, $C_{11}H_{18}O_4$, which melts at 172—173°. Its constitution, assuming that of the diketone, may be represented by the formula

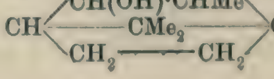


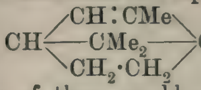
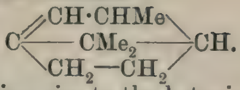
$$\mathrm{CO_2H\cdot CH}\left\langle\begin{array}{c}\mathrm{-CMe_2-}\\ \mathrm{CH_2\cdot CH_2}\end{array}\right\rangle\mathrm{CH\cdot CHMe\cdot CO_2H.}$$

Crude fenchonitrile, obtained by warming fenchonoxime with dilute sulphuric acid, consists of two isomerides, which behave differently towards sodium ethoxide, the one yielding an amide, whilst the other is completely hydrolysed and furnishes solid fencholenic acid, a compound crystallising from acetone or light petroleum and melting at 68—70° (compare Cockburn, Trans., 1899, **75**, 501). The liquid and solid modifications of fencholenic acid are designated by the symbols α and β respectively. Both α- and β-acids yield brominated lactones by the action of sodium hypobromite on cold solutions of their sodium salts, these derivatives melting respectively at 76° and 80°. *β-Fencholenamide* melts at 85—86°, the melting point of its isomeride being 113—114°.

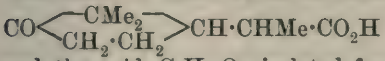
[With EDGAR NEUMANN.]—A strongly lævorotatory fenchyl chloride is produced by mixing together at low temperatures in light petroleum, phosphorus pentachloride and pure *Dl*-fenchyl alcohol, removing the phosphorus oxychloride produced with cold water, and distilling the dried residue in a vacuum. The hydrocarbon obtained by the action of aniline on this chloride consists chiefly of *Dl*-fenchene. When the reagents are mixed without cooling, and the action completed on the water-bath, a dextrorotatory fenchyl chloride is produced, and this yields a fenchene having a rotation of the same sign.

The *ether*, $C_{10}H_7\cdot OEt$, produced by heating *Dd*-fenchene with alcoholic sulphuric acid, boils at 200—201°, and on treatment with metallic sodium yields the sodium derivative of the alcohol, $C_{10}H_{17}\cdot OH$. This alcohol melts at 61°, and is identical with the *iso*fenchyl alcohol discovered by Bertram and Helle (compare Abstr., 1900, i, 398). Different specimens of crude fenchene vary greatly in their behaviour towards permanganate solution, and generally yield a mixture of *Dl*- and *Dd*-hydroxyfenchenic acids, the lævorotatory isomeride predominating. Some samples of the hydrocarbon contain readily oxidisable substances, and in this case the product of oxidation is a complex mixture consisting of the two hydroxyfenchenic acids, together with acids of the acetic series and a *ketonic acid*, $C_8H_{12}O_3$, this compound being identified by means of its *semicarbazone*, $C_8H_{12}O_2\cdot CON_3H_3$, and its *silver* salt, $C_8H_{11}O_3Ag$.

Fenchyl alcohol,  $\mathrm{CH}\left\langle\begin{array}{c}\mathrm{CH(OH)\cdot CHMe}\\ \mathrm{CMe_2}\\ \mathrm{CH_2-CH_2}\end{array}\right\rangle\mathrm{CH}$, should, on dehydration, yield fenchenes corresponding with the formulæ

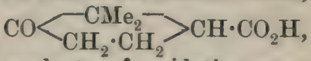
I.  and II. 

The latter of these would on oxidation give rise to the ketonic acids,



$$CO{<}\substack{CMe_2\\CH_2\cdot CH_2}{>}CH\cdot CHMe\cdot CO_2H$$

and

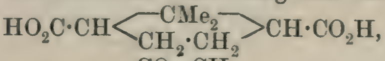


$$CO{<}\substack{CMe_2\\CH_2\cdot CH_2}{>}CH\cdot CO_2H,$$

and the acid, $C_8H_{12}O_3$, isolated from the products of oxidation, may possibly have the constitution represented by the second of these formulæ.

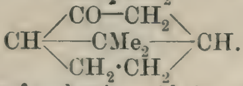
The *acetyl* derivative of *Dl*-hydroxyfenchenic acid melts at 109—110°; the acid itself on oxidation yields *Dd*-fenchocamphorone (Abstr., 1899, i, 488; 1900, i, 241). This substance, when reduced with sodium in ethereal solution, gives rise to fenchocamphorol and the corresponding *pinacone*, $C_{18}H_{30}O_2$, melting at 192—193°.

On reducing the fenchocamphonitrile with sodium and alcohol, the base $C_9H_{15}\cdot NH_2$ is obtained, and is identified by means of its platinichloride and carbamide. An isomeric *base*, produced by the direct reduction of fenchocamphoronoxime with sodium and amyl alcohol, boils at 196—199°, and solidifies at low temperatures. Its *hydrochloride*, $C_{19}H_{15}\cdot NH_2,HCl$, is very stable, and crystallises from a mixture of ether and alcohol. The acid, $C_9H_{14}O_4$, produced by oxidising fenchocamphorone with nitric acid, yields the *anhydride*, $C_9H_{12}O_3$, and the *monoanilide*, melting respectively at 176—177° and 211°. These compounds agree in their properties with the corresponding derivatives of camphopyric acid (compare Marsh and Gardner, Trans., 1896, **69**, 74) and hence the two acids are identical. Assuming that camphopyric acid has the constitution

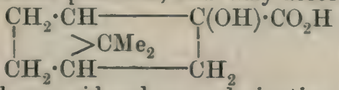


$$HO_2C\cdot CH{<}\substack{CMe_2\\CH_2\cdot CH_2}{>}CH\cdot CO_2H,$$

then that of fenchocamphorone should be

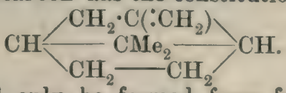


The constitution of *Dl*-hydroxyfenchenic acid (m. p. 152°) depends on those of its degradation products, and may accordingly be represented by the formula



$$\begin{array}{lll} CH_2\cdot CH & \text{———} & C(OH)\cdot CO_2H \\ | & >CMe_2 & | \\ CH_2\cdot CH & \text{———} & CH_2 \end{array}$$

, and although such a substance may be considered as a derivative of the fenchene of formula I, yet its formation is more readily explained on the assumption that the hydrocarbon has the constitution

III. 

This hydrocarbon could only be formed from fenchyl alcohol if a shifting of the double linking in formulæ I and II occurs; if this possibility be admitted, then four other structurally dissimilar fenchenes are theoretically possible.

Dd-Hydroxyfenchenic acid (m. p. 138°) yields an *acetyl* derivative crystallising in prisms and melting at 122—124°.

Dl-Fenchocamphorone forms an oxime and a nitrile like its *Dd*-isomeride, but differs from this substance in not yielding a camphopyric acid with dilute nitric acid. The principal product of this action is an acid whose mono- and di-anilides agree in properties with those of *as*-dimethylsuccinic acid; there is, however, a discrepancy in the melting points of the anhydrides, that from the acid derived from *Dl*-fenchocamphorone melting at 125—130°, whilst *as*-dimethylsuccinic anhydride melts at 29°.

Since *Dd*-fenchene also yields a hydroxyfenchenic acid, it may be a stereoisomeride of *Dl*-fenchene; on the other hand, the two fenchocamphorones behave quite differently on oxidation with nitric acid, and, moreover, the hydrocarbons themselves are not attacked with equal readiness by permanganate solutions, so that it is quite possible that the two isomerides may be structurally dissimilar. G. T. M.

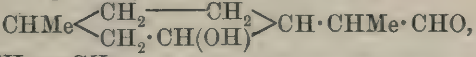
Ethereal Oil of Buchu Leaves, and the Constitution of its Constituents. By IWAN KONDAKOFF and N. BACHTSCHÉEFF (*J. pr. Chem.*, 1901, [ii], **63**, 49—77. Compare Bialobrczeski, Abstr., 1897, i, 433).—The best samples of oil from *Barosma betulina* and *B. serratifolia* contain about 10 per cent. of hydrocarbons, $C_{10}H_{16}$, 60 per cent. of a ketomenthone, $C_{10}H_{18}O$, and 5 per cent. of diosphenol.

The fraction comprising the hydrocarbons contained neither sylvestrene nor carvestrene, and its boiling point is higher than that of phellandrene. On brominating it in the cold, and afterwards fractionally crystallising the product from alcohol-ether, tetrabromides were obtained indicating the presence of *d*-limonene and dipentene in the original oil.

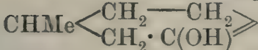
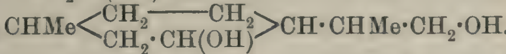
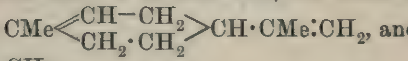
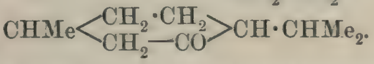
The ketomenthone, $C_{10}H_{18}O$, is a colourless liquid with a peppermint-like odour; it boils at 208·5—209·5° under 760 mm. pressure, and has a sp. gr. 0·9004 at 19°/19°, $[\alpha]_D$ −16°6′, n_D 1·45359, and molecular refraction 46·28. Its oxime is liquid and optically active. On reduction with sodium in methyl alcoholic solution, it yielded a solid and a liquid *menthol*. The former crystallised in needles, melted at 38·5—39°, had a sp. gr. 0·9006 at 32°/32°, and n_D 1·45869 at 32°, and dissolved in all organic solvents. The *benzoate* melted at 82°; when treated with phosphoric oxide, this menthol was converted into a menthene which boiled at 166·5—168·5° under 785 mm. pressure, and had a sp. gr. 0·8112 at 19°/19°, n_D 1·45109 and $[\alpha]_D$ −13°46′. The isomeric liquid menthol boiled at 106·5—109° under 18 mm. pressure, had a sp. gr. 0·9041 at 21·6°/21·6°, $[\alpha]_D$ +26°30′ and n_D 1·461793, and gave a menthene of lower lævorotation than that described by Berkenheim (Abstr., 1892, 866), or Masson and Reychler (*Ber.*, 1896, **29**, 1843). The solid menthol is not identical with the natural substance, and the liquid isomeride seems to be new.

Diosphenol, $C_{10}H_{18}O_2$, or $C_{10}H_{16}O_2$, an inactive phenolic aldehyde, melted at 82°. On reduction with hydriodic acid and phosphorus at 210°, it yielded a hydrocarbon, $C_{10}H_{20}$, of the hexahydrocymene series; this boiled at 165—168° under 762 mm. pressure, had a sp. gr. 0·7916 at 21·6°/21·6°, and n_D 1·43539. On reduction with sodium and alcohol, it gave (1) an inactive *menthol*, which was volatile with steam, boiled at 215—216° under 763 mm. pressure, and had a sp. gr. 0·9052 at 20°/20° and n_D 1·464456. The inactive *iodide* obtained from this menthol boiled at 126·5° under 17 mm. pressure, and with alcoholic potassium hydroxide yielded an active *menthene*, which boiled at 168—169°, and had a sp. gr. 0·8158 at 19·8°/19·8°, n_D 1·45909 and $[\alpha]_D$ −37′. (2) An active, odourless *glycol*, $C_{10}H_{20}O_2$, which crystallised in colourless needles, melted at 92°, had a sharp, cooling taste, and was not volatile with steam. When heated with hydriodic acid at 100° for 6 hours, it yielded a liquid *menthyl iodide*, $C_{10}H_{19}I$, which boiled at 112—114° under 9 mm. pressure, and had a sp. gr. 1·359 at 20·6°/20·6° and n_D 1·520771. With hydriodic acid at 185°, it yielded the same hexahydrocymene as does diosphenol itself. (3) A liquid *glycol*, stereoisomeric with the preceding compound; it boiled at 141·5—145° under 13 mm. pressure, and had a sp. gr. 0·995 at 21·6°/21·6°, and n_D 1·47877.

Diosphenol, when heated with phosphoric oxide, yields propylene and *m*-cresol. It probably has the constitution



$$CHMe{<}\begin{array}{l}CH_2\text{——}CH_2\\ CH_2\cdot CH(OH)\end{array}{>}CH\cdot CHMe\cdot CHO,$$

or  $CHMe{<}\begin{array}{l}CH_2\text{—}CH_2\\ CH_2\cdot C(OH)\end{array}{\geqslant}C\cdot CHMe\cdot CHO$, and the glycol derived from it will be  $CHMe{<}\begin{array}{l}CH_2\text{——}CH_2\\ CH_2\cdot CH(OH)\end{array}{>}CH\cdot CHMe\cdot CH_2\cdot OH$. With regard to the constitution of the other constituents of buchu oil, the authors suggest that the hydrocarbon is  $CMe{\leqslant}\begin{array}{l}CH\text{—}CH_2\\ CH_2\cdot CH_2\end{array}{>}CH\cdot CMe{:}CH_2$, and the ketomenthone,  $CHMe{<}\begin{array}{l}CH_2\cdot CH_2\\ CH_2\text{—}CO\end{array}{>}CH\cdot CHMe_2$. W. A. B.

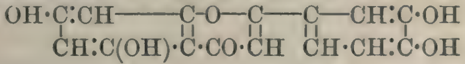
Constitution of Gallotannin. By HENRI POTTEVIN (*Compt. rend.*, 1901, **132**, 704—706).—Commercial gallotannin when purified by ether extraction consists essentially of a glucoside of gallic acid; it yields this acid and dextrose when hydrolysed by tannase, and when heated at 110° in a sealed tube with very dilute hydrochloric acid it yields the same sugar and digallic acid (compare this vol., i, 179).

G. T. M.

Synthesis of Luteolin. By STANISLAUS VON KOSTANECKI (*Bull. Soc. Ind. Mulh.*, 1901, **71**, 35—41).—By the action of ethyl veratrate, $C_6H_3(OMe)_2\cdot CO_2Et$, on *s*-trimethoxyacetophenone, $C_6H_2(OMe)_3\cdot CO\cdot CH_3$, a *pentamethoxybenzoylacetophenone*,

$$C_6H_2(OMe)_3\cdot CO\cdot CH_2\cdot CO\cdot C_6H_3(OMe)_2,$$

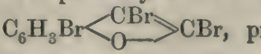
is produced, which is converted into luteolin by heating with hydriodic acid, when five methyl groups and a mol. of water are eliminated. The constitution of luteolin is thus shown to be

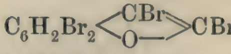


$$\begin{array}{l}OH\cdot C{:}CH\text{——}C\text{-}O\text{—}C\text{—}C\text{—}CH{:}C\cdot OH\\ CH{:}C(OH)\cdot C\cdot CO\cdot CH\;\;CH\cdot CH{:}C\cdot OH\end{array}$$

T. M. L.

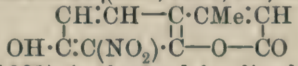
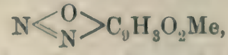
Bromo-derivatives of Coumarone. By HUGO SIMONIS (*Ber.*, 1901, **34**, 781—784).—The tribromocoumarone produced by the action of bromine on 1 : 2-dibromocoumarone (Stoermer, Abstr., 1901, i, 654) is not the 1 : 2 : 4-compound, but is probably the 1 : 2 : 6-isomeride.

1 : 2 : 4-*Tribromocoumarone*,  $C_6H_3Br{<}\begin{array}{l}CBr\\ O\end{array}{\geqslant}CBr$, prepared by the action of bromine on 1 : 4-dibromocoumarone dissolved in carbon disulphide, crystallises in needles and melts at 115°. 1 : 2 : 4 : 6-*Tetra-*

bromocoumarone,  $C_6H_2Br_2<\begin{matrix}CBr\\O-\!-\end{matrix}>CBr$, prepared by the slow action of bromine on 1 : 4 : 6-tribromocoumarone, crystallises in white needles and melts at 134°. T. M. L.

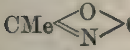
Coumarilic Acid and its Derivatives. By Richard Stoermer and G. Calov (*Ber.*, 1901, **34**, 770—775).—The chief product of the action of bromine on coumarilic acid is Stoermer and Richter's tribromocoumarone (Abstr., 1900, i, 654), and a pure monobromocoumarone could not be isolated. The *amide*, $C_9H_7O_2N$, prepared by the action of ammonia on the ethyl ester, forms white flakes and melts at 159°. The *nitrile*, C_9H_5ON, crystallises from dilute alcohol in long, silky needles, melts at 36°, and smells like cinnamon. The acid *chloride* melts at 52°, smells like bitter almond oil, and is decomposed by warming with water. The *phenyl* ester, $C_{15}H_{10}O_3$, crystallises from alcohol in long, white needles and melts at 101°. The *anilide* forms small, yellowish-white needles and melts at 159°. The *hydrazide*, $C_9H_8O_2N_2$, crystallises from dilute alcohol in white, felted needles, melts at 172°, and reduces Fehling's solution and ammoniacal silver nitrate. The *azoimide*, $C_9H_5O_2N_3$, crystallises from dilute alcohol in small, white flakes and melts at 109°. *Urethylcoumarone*, $C_8H_5O{\cdot}NH{\cdot}CO_2Et$, prepared by boiling the azoimide with alcohol, crystallises from alcohol in large, glistening, white scales and melts at 141°; it is hydrolysed by hydrogen chloride and by potassium hydroxide to *o*-hydroxyphenylacetic acid.

Acetylcoumaroneoxime, $C_{10}H_9O_2N$, crystallises from dilute alcohol in white, silky needles and melts at 150°. *Dicoumarylketoxime*, $C_{17}H_{11}O_3N$, forms yellowish-white, felted needles, and melts and decomposes at 222—223°. Neither of these compounds undergoes isomeric change smoothly when acted on by phosphorus pentachloride. T. M. L.

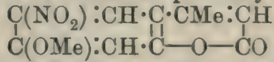
Derivatives of 4-Methylumbelliferone. By Hans von Pechmann and Julius Obermiller (*Ber.*, 1901, **34**, 660—674).—8-Nitro-4-methylumbelliferone,  $\begin{matrix}CH{:}CH-\!-C{\cdot}CMe{:}CH\\ \vert \qquad\qquad \Vert \qquad\quad \vert\\ OH{\cdot}C{:}C(NO_2){\cdot}C-\!-O-\!-CO\end{matrix}$ (von Pechmann and Cohen, Abstr., 1884, 1331), is obtained by dissolving crude 4-methylumbelliferone in strong sulphuric acid, and nitrating it below 0° with a mixture of strong nitric and sulphuric acids. When crystallised from nitrobenzene, it melts at 228—229°, from a mixture of nitrobenzene and alcohol (2 : 1) at 255°. When heated with strong ammonia at 80—85°, it yields 2-nitroresorcinol, the yellowish *dibenzoyl* derivative of which melts at 138—139°. It is reduced by stannous chloride and alcoholic hydrochloric acid to yellow 8-amino-4-methylumbelliferone, which decomposes and melts completely below 270°. Nitrous acid converts this amino-compound, at 0—5° and in the dark, into 4-*methylumbelliferone*-8-*diazoanhydride*,  $N\ll\begin{matrix}O\\N\end{matrix}>C_9H_3O_2Me$, which was mistaken by von Pechmann and Cohen for a nitroso-derivative. It forms yellowish-red crystals, and perhaps exists in two varieties decomposing at 173—175° and 135—136° respectively; the corresponding *picrates* are red, and melt at 176—180° and 160—165°. It is stable in the dark, but not in the light; it unites with phenols, but not with dimethylaniline, forming azo-dyes; it yields a *hydrochloride*, and with potassium sulphite it forms *potassium-4-methylumbelliferone-8-diazosulphonate*, which is red, and crystallises with $2H_2O$; the solution of the hydrochloride yields the diazoanhydride when it is precipitated with sodium carbonate or acetate, 4-methylumbelliferone when it is heated with copper powder, and 8-*hydrazino-4-methylumbelliferone* when it is reduced with stannous chloride.

When the amino-compound is heated with acetic anhydride and sodium acetate, *triacetyl-8-amino-4-methylumbelliferone*,

$$NAc_2{\cdot}C_9H_3O_2Me{\cdot}OAc,$$

melting at 183—184° is obtained. When this is dissolved in alcoholic potash and then precipitated with hydrochloric acid, the *diacetyl* compound, $NAc_2{\cdot}C_9H_3O_2Me{\cdot}OH$, melting at 261—262° is formed. This is hydrolysed by cold, strong hydrochloric acid to the *monoacetyl* compound, $NHAc{\cdot}C_9H_3O_2MeOH$, melting at 290°, whilst the hot acid hydrolyses it to 8-amino-4-methylumbelliferone. These acetyl derivatives lose acetic anhydride, acetic acid, or water respectively when heated, and in addition form *ethenyl-8-amino-4-methylumbelliferone*,  $CMe\lt\substack{O\\N}\gt C_9H_3O_2Me$, which melts at 202—203°, and readily regenerates the monoacetyl compound under the influence of hydrochloric acid. By boiling nitromethylumbelliferone with acetic anhydride and sodium acetate, 8-*nitro-4-methylumbelliferone acetate*, $NO_2{\cdot}C_9H_3O_2Me{\cdot}OAc$, melting at 165—166°, is obtained. Reduction of this with stannous chloride does not give the expected aminohydroxy-compound; the monoacetylamino-compound described above is obtained instead, and by very careful work the ethenylamino-compound can be isolated as an intermediate product.

8-*Nitro-4-methylumbelliferone methyl ether*, $NO_2{\cdot}C_9H_3O_2Me{\cdot}OMe$, is obtained by heating nitroumbelliferone with methyl-alcoholic sodium methoxide and methyl iodide at 100°; it is yellowish, melts at 230°, and can be reduced with stannous chloride and hydrochloric acid to yellowish 8-*amino-4-methylumbelliferone methyl ether*, which melts at 161°.

When β-methylumbelliferone methyl ether (von Pechmann and Duisberg, Abstr., 1884, 66) is nitrated in the manner already given, in addition to the methyl ether just described there is obtained an isomeride which is less soluble in a mixture of nitrobenzene and alcohol, is pale yellow, and melts at 281—282°. This is probably 6-*nitro-4-methylumbelliferone methyl ether*,  $\begin{array}{l} C(NO_2){:}CH{\cdot}C{\cdot}CMe{:}CH \\ C(OMe){:}CH{\cdot}C—O—CO \end{array}$; when reduced, it yields 6-*amino-4-methylumbelliferone methyl ether*, which melts at 221—222°.

C. F. B.

Arylthiosulphonates of Organic Bases. By JULIUS TROEGER and OTTO LINDE (*Arch. Pharm.*, 1901, **239**, 121—145).—Attention is drawn to the close analogy between arylthiosulphonates and thiosulphates, to which the former stand in the same relation as the arylsulphinates to the sulphites. A number of arylthiosulphonates of organic bases, chiefly alkaloids, is described. These were prepared by mixing aqueous solutions of the potassium arylthiosulphonate and a salt (usually the hydrochloride) of the base; they separated sometimes in crystals, but more often as oils, which usually solidified after a time. The salts prepared are enumerated below; when they were analysed their composition is given, B standing for 1 mol. of the base, A for 1 mol. of the acid, $C_6H_5 \cdot SO_2 \cdot SH$, $C_7H_7 \cdot SO_2 \cdot SH$, or $C_{10}H_7 \cdot SO_2 \cdot SH$, as the case may be. Benzidine *p*-toluenethiosulphonate forms a noteworthy exception to the general rule, as it contains only 1 mol. of acid per 1 mol. of the di-acid base.

	Benzenethiosulphonate.	*p*-Toluenethiosulphonate.	α-Naphthalenethiosulphonate.	β-Naphthalenethiosulphonate.
Berberine, $C_{20}H_{17}O_4N$	B,A	B,A,H_2O	B,A	B,A
Brucine, $C_{23}H_{26}O_4N_2$	B,A	B,A	B,A	B,A
Strychnine, $C_{21}H_{22}O_2N_2$	B,A	B,A	B,A	B,A
Morphine, $C_{17}H_{19}O_3N$	B,A	B,A	B,A	B,A
Codeine, $C_{18}H_{21}O_3N$	—	B,A	B,A	B,A
Cinchonine, $C_{19}H_{22}ON_2$	—	B,A	—	B,A
Cinchonidine, $C_{19}H_{22}ON_2$	—	—	B,A	—
Quinine, $C_{20}H_{24}O_2N_2$	—	B,A	—	—
Quinidine, $C_{20}H_{24}O_2N_2$	—	—	—	B,A
Guanidine, CH_5N_3	B,A	B,A	B,A	B,A
Aniline, C_6H_7N	—	B,A	—	B,A
Phenylhydrazine, $C_6H_8N_2$	—	—	B,A	B,A
m-Phenylenediamine, $C_6H_8N_2$	—	B,2A	—	B,2A
p-Phenylenediamine, $C_6H_8N_2$	B,2A	B,2A	B,2A	B,2A
Benzidine, $C_{12}H_{12}N_2$	B,2A	B,A	B,2A	B,2A
Tolidine, $C_{14}H_{16}N_2$	B,2A	B,2A	B,2A	B,2A

C. F. B.

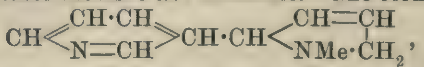
Cinchonine. By ÉMILE JUNGFLEISCH and EUGÈNE LÉGER (*Compt. rend.*, 1901, **132**, 828—830. Compare this vol., i, 287).—Specimens of crude basic cinchonine sulphate always contain notable quantities of the hydrocinchonine salt, sometimes to the extent of 20 per cent. The latter base is only slowly eliminated by fractional crystallisation of the normal salt from 95 per cent. alcohol, each crystallisation removing one quarter of the hydrocinchonine salt present in the material. A specimen of cinchonine sulphate containing only 1 per cent. of the hydrocinchonine salt is less soluble in water at different temperatures than the salt of the crude mixture of bases. Purified cinchonine melts at 264·3° the melting points of specimens of the crude base varying from 248 to 268·8°; it has a greater optical activity than a mixture of the two alkaloids, hydrocinchonine being less active than cinchonine and having $[\alpha]_D$ 229·6°. G. T. M.

Echinopsine a new Crystalline Alkaloid. By MAURITS GRESHOFF (*Rec. Trav. Chim.*, 1900, **19**, 360—363).—*Echinopsine*, $C_{11}H_9ON$, is present in 15 different species of the genus *Echinops*, and is best obtained from the seeds of *Echinops Ritro*, L., by removing their oil with light petroleum and then extracting with alcohol; it dissolves in 60 parts of water at 15°, in 6 at 100°, crystallises with $1H_2O$ in rhombs, or when anhydrous, in tufts of needles. It melts at 152° and does not decompose at 350°. The *hydrochloride*, $C_{11}H_9ON,HCl,2H_2O$, forms large, rhombic crystals; the *sulphate*, with either 2 or 8 H_2O, forms long needles, and the *nitrate* contains $3H_2O$; the *oxalate*, with $4H_2O$, forms good crystals, and the *picrate* melts at 215°. The *mercurichloride* melts at 204° and the *mercuriodide* at 178°; with a solution of iodine, a crystalline *compound* is formed, which melts at about 135°, and can be used to localise the alkaloid in the tissues of *Echinops*. The toxic action of the alkaloid is similar to, but not identical with, that of a mixture of strychnine and brucine. Its composition is that of a phenylpyridone, but it is not identical with any known phenylpyridone; on reduction with zinc dust in a stream of hydrogen, it yields an *amine* with an odour of pyridine, but not identical with any of the known phenylpyridines. Fused with potash, it yields ammonia and pyridine.

The following compounds are also present in *Echinops*: *β-echinopsine* which melts at 135°, and *echinopseine* and *echinopsfluorescin*, of which traces only were isolated. W. A. D.

New Alkaloids from Tobacco. By AMÉ PICTET and A. ROTSCHY (*Ber.*, 1901, **34**, 696—708).—The crude nicotine obtained by distilling a concentrated aqueous extract of tobacco leaves with steam, contains about 0·5 per cent. of its weight of an isomeride, *nicotimine*, $C_{10}H_{14}N_2$; this is a secondary base and is separated by converting it into its *nitroso*-derivative, removing the nicotine by distillation under diminished pressure, boiling the residue with concentrated hydrochloric acid, and converting the regenerated base into its *benzoyl* derivative. The latter is a bright yellow oil which boils above 350°, does not solidify at $-10°$, and on hydrolysis with concentrated hydrochloric acid yields nicotimine as a colourless liquid boiling at 250—255°. The base is easily soluble in water, is volatile with steam, and yields a white, crystalline, deliquescent *hydrochloride*; the yellow *platinichloride* becomes greyish at 270°, but does not melt at 290°; the *aurichloride* decomposes at 182—185°, the *mercurichloride* at 190°, whilst the *picrate* forms thick prisms and melts at 163°. These facts show that nicotimine is not identical with Pinner's metanicotine (Abstr., 1894, i, 388).

The aqueous extract remaining after the removal of the nicotine and its isomeride contains two alkaloids, nicoteine and nicotelline, which are not volatile with steam. *Nicoteine*, $C_{10}H_{12}N_2$, is a colourless liquid which is readily soluble in water and in ether, boils at 266—267° (uncorr.), and does not solidify at $-79°$; it has a sp. gr. 1·0778° at 12·5°/4°, n_D 1·56021 at 14°, a mol. refraction 48·01, and $[\alpha]_D$ $-46·41°$. The *dihydrochloride*, is amorphous and has $[\alpha]_D$ $-8·27°$; the *platinichloride*, $C_{10}H_{12}N_2,H_2PtCl_6$, forms yellow crystals and does not melt at 280°, the *aurichloride* becomes grey at 150° and melts and decomposes at 186°, and the *picrate* forms large, transparent prisms and melts at 165°; two *mercurichlorides* are described, one melting at about 115° and the other at 215° with decomposition. The *dimethiodide*, $C_{10}H_{12}N_2,2MeI$, is a yellow oil which cannot be made to crystallise. Attempts to convert nicoteine into nicotine by reduction failed; tin and hydrochloric acid are without action, whilst sodium and alcohol yield a product which is not volatile with steam. When the *bromo*-derivative of the base is reduced by tin and hydrochloric acid (compare Abstr., 1898, i, 688, and 1900, i, 685), a base is obtained which is volatile with steam but is neither nicotine nor nicoteine. The formula



$$CH{<}\begin{matrix}CH\cdot CH\\ N{=}CH\end{matrix}{>}CH\cdot CH{<}\begin{matrix}CH{=}CH\\ NMe\cdot CH_2\end{matrix},$$

given to the base shows it to be closely allied with dihydronicotyrine (Pictet and Crépieux, Abstr., 1898, i, 688) and dehydronicotine (Pinner and Wolffenstein, Abstr., 1892, 1010; 1895, ii, 308), and explains the following facts. (1) Nicoteine on oxidation with nitric acid yields nicotinic acid; (2) it decolorises aqueous potassium permanganate in presence of sulphuric acid; (3) its acid solutions respond to the tests for a pyrrole derivative.

Nicotelline, $C_{10}H_8N_2$, is only very slightly soluble in water and ether, and is best extracted from the original aqueous solution by chloroform; it crystallises from this solvent on adding light petroleum in small, white needles, melts at 147—148° and boils slightly above 300°; unlike the other alkaloids of tobacco, its aqueous solution is neutral to litmus. It does not appear to be a pyrrole derivative, and does not decolorise potassium permanganate in presence of sulphuric acid; the *hydrochloride* is easily soluble in water and the *platinichloride* sparingly so; the *aurichloride* sinters and decomposes at about 170°, and the *mercurichloride* melts at 200—201°. Nicotelline differs from the other alkaloids of tobacco in yielding a very sparingly soluble *dichromate*.

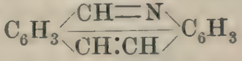
W. A. D.

Pilocarpine. By Adolf Pinner and Erich Kohlhammer (*Ber.*, 1901, **34**, 727—736. Compare Abstr., 1900, i, 456, 685, and Jowett, Trans., 1900, **77**, 494, 851, and Abstr., i, 686).—The authors confirm their statement that the potassium and barium salts of piluvic acid are derived from an acid $C_8H_{14}O_6$, although the *acid* itself, a yellowish, non-crystallisable syrup, has the formula $C_8H_{12}O_5$, and the ethyl ester the formula $C_8H_{10}O_5Et_2$; the *amyl* ester, $C_8H_{10}O_5(C_5H_{11})_2$ boils at 192° under 25 mm. pressure and is somewhat unstable.

In addition to piluvic acid, the oxidation of pilocarpine with aqueous potassium permanganate apparently gives rise to nitrogenous acids, a small quantity of *barium* salt, $C_{11}H_{15}O_5NBa$ being isolated.

When barium pilocarpoeate is oxidised with 1 per cent. aqueous potassium permanganate (corresponding with 5O), it yields iso*hydrochelidonic acid*, $C_7H_{10}O_5$, which crystallises from its aqueous solution in colourless, lustrous needles and melts at 145°; the *barium* salt, $C_7H_8O_5Ba,H_2O$, forms small leaflets and is sparingly soluble, and the *lead* salt, $C_7H_8O_5Pb$, is anhydrous. Whether the acid is identical with Volhard's hydrochelidonic acid (Abstr., 1890, 30; 1892, 432) is uncertain; the melting point is the same, but Volhard's barium salt contained $2-2\frac{1}{2}H_2O$. In addition to the *iso*hydrochelidonic acid isolated, a potassium salt was obtained which was either potassium malonate or a molecular mixture of potassium oxalate and succinate.

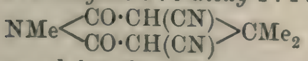
W. A. D.

Thebenidine. By EDUARD VONGERICHTEN (*Ber.*, 1901, **34**, 767—770).—The base *thebenidine*, which is produced together with pyrene on distilling thebenine with zinc dust, is insoluble in water, but crystallises from benzene, melts at 144—148°, and is not oxidised by chromic acid; it forms a yellow *platinichloride*, $(C_{15}H_9N)_2,H_2PtCl_6$; the *methiodide*, $C_{16}H_{12}NI$, forms yellow prisms, melts at about 240° and cannot be methylated further. The formula  $C_6H_3\left\langle\begin{matrix}CH{=}N\\CH{:}CH\end{matrix}\right\rangle C_6H_3$ is suggested for the base. T. M. L.

Theobromine and Caffeine and the Salts they Form. By THEODOR PAUL (*Arch. Pharm.*, 1901, **239**, 48—90).—One part of theobromine requires for its solution 3282 parts of (carefully purified) water at 18°; of *N*/4 hydrochloric acid, 2125; of *N* hydrochloric acid, 1205; of *N*/10 sodium hydroxide, 57·02; of *N*/4 sodium hydroxide, 22·93 parts. As the solubility in acid is so very little more than in water, it is evident that the hydrochloride is very largely dissociated hydrolytically, and that the basic character of theobromine is very feeble. On the other hand, the large increase of solubility in sodium hydroxide indicates that the sodium salt is much less dissociated hydrolytically, and that the acid character of theobromine is much more marked than the basic. The dissociation constant, *k*, of theobromine for its dissociation into $C_7H_8\overset{-}{O}_2N_4\cdot OH$ and $\overset{+}{H}$, is $1\cdot33 \times 10^{-8}$, and the degree of its dissociation in the solution saturated at 18° is 0·0027. The constant for its dissociation into $C_7H_8\overset{+}{O}_2N_4\cdot H$ and $\overset{-}{OH}$ is $1\cdot5 \times 10^{-14}$. As an acid, then, theobromine is about of equal strength with the substituted phenols and the cresols, and is about 100 times weaker than uric acid. As a base, it is about 60 times weaker than betaine, and about 40,000 times weaker than aniline. The molecular conductivity of theobromine in aqueous solution saturated at 18°, is 0·9; it may be regarded as due only to the acid dissociation of the substance. C. F. B.

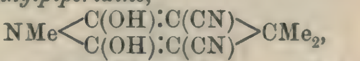
Synthesis of Derivatives of Pyridine and of Trimethylenepyrrole. By ICILIO GUARESCHI (*Mem. Real. Accad. Sci. Torino*, 1901, [ii], **50**, 235—288. Compare Abstr., 1897, i, 168; Grande, Abstr., 1898, i, 272; Quenda, Abstr., 1898, i, 272; Pasquali, Abstr., 1898, i, 272; Sabbatani, Abstr., 1898, i, 273; Guareschi, Abstr., 1898, i, 274; 1900, i, 52, and 558; Guareschi and Grande, Abstr., 1900, i, 111 and 112).—This paper deals with the formation of ring compounds by the action of various ketones on ethyl cyanoacetate in presence of either ammonia or an amine. In addition to the work already published (*loc. cit.*), the following new results have been obtained.

3 : 5-*Dicyano*-2 : 6-*dioxy*-1 : 4 : 4-*trimethylpiperidine*,



$$NMe\left\langle\begin{matrix}CO\cdot CH(CN)\\CO\cdot CH(CN)\end{matrix}\right\rangle CMe_2$$

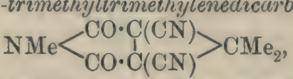
or



$$NMe\left\langle\begin{matrix}C(OH){:}C(CN)\\C(OH){:}C(CN)\end{matrix}\right\rangle CMe_2,$$

prepared by the interaction of acetone (1 mol.), methyl or ethyl cyanoacetate (2 mols.) and an alcoholic solution of methylamine (3 mols.) with subsequent acidification, separates from dilute alcohol in large, colourless, acicular crystals which melt at 163—163·5°, and when heated rapidly, volatilise unchanged; it is very soluble in pyridine, less so in alcohol or boiling water, and very slightly in ether. Its aqueous solution has a marked acid reaction, and when neutralised with ammonia gives a voluminous white precipitate with silver nitrate solution. It contains two hydrogen atoms replaceable by silver; the *mono-silver*, $C_{10}H_{10}O_2N_3Ag$ [Ag = 2 or 3], and the *di-silver*, $C_{10}H_9O_2N_3Ag_2$ [Ag : Ag = 3 : 5 or 2 : 6], derivatives are both white precipitates. The *dibromo*-derivative separates from dilute acetic acid solution in colourless laminæ or short prisms which melt at 144—145°, and decompose at about 200° with evolution of bromine. On heating the dibromo-compound with excess of 50 per cent. acetic acid, it yields

3 : 5-*Dicyano*-1 : 4 : 4-*trimethyltrimethylenedicarbonimide*,



$$\mathrm{NMe}{<}\begin{array}{l}\mathrm{CO\cdot C(CN)}\\ \qquad | \\ \mathrm{CO\cdot C(CN)}\end{array}{>}\mathrm{CMe_2},$$

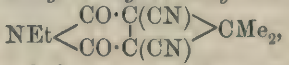
which separates from alcohol in acicular crystals melting at 241·5°, and dissolves readily in pyridine, less so in alcohol, and to a slight extent in water; it sublimes in the form of a bulky mass of slender needles, gives a neutral aqueous solution, not precipitated by silver nitrate in presence of ammonia, and does not absorb bromine.

3 : 5-*Dicyano*-2 : 6-*dioxy*-4 : 4-*dimethyl*-1-*ethylpiperidine*,

$$C_5NH_2Me_2EtO_2(CN)_2,$$

obtained by the interaction of acetone, ethyl cyanoacetate and alcoholic ethylamine, separates from dilute alcohol in hard, sparkling, colourless crystals melting at 110·5—111·5°; it is very soluble in pyridine or alkali solutions, less so in alcohol, and only to a slight extent in water, giving an acid solution. Its *dibromo*-derivative separates from dilute acetic acid in colourless, prismatic crystals which melt at 130—132° and are soluble in acetic acid. Heated with 50 per cent. acetic acid, the dibromo-compound is converted into

3 : 5-*Dicyano*-4 : 4-*dimethyl*-1-*ethyltrimethylenedicarbonimide*,



$$\mathrm{NEt}{<}\begin{array}{l}\mathrm{CO\cdot C(CN)}\\ \qquad | \\ \mathrm{CO\cdot C(CN)}\end{array}{>}\mathrm{CMe_2},$$

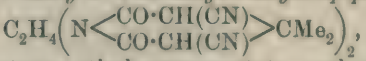
which separates in hard, heavy crystals melting at 211° and subliming in very light, colourless needles; it is very soluble in pyridine, slightly so in water, and has a neutral reaction.

3 : 5-*Dicyano*-2 : 6-*dioxy*-1-*benzyl*-4 : 4-*dimethylpiperidine*,

$$C_7H_7\cdot C_5NH_2Me_2O_2(CN)_2,$$

prepared from acetone, ethyl cyanoacetate, and alcoholic benzylamine, separates from dilute alcohol in long, silky needles which melt at 149—150° and dissolve in potassium hydroxide solution. It has an acid reaction and when neutralised with sodium hydroxide solution behaves like a monobasic acid.

3 : 5-*Dicyano*-2 : 6-*dioxy*-4 : 4-*dimethyl*-1-*ethylenepiperidine*,



$$\mathrm{C_2H_4}\left(\mathrm{N}{<}\begin{array}{l}\mathrm{CO\cdot CH(CN)}\\ \mathrm{CO\cdot CH(CN)}\end{array}{>}\mathrm{CMe_2}\right)_2,$$

obtained from acetone, ethyl cyanoacetate, and alcoholic ethylenediamine, crystallises from dilute alcohol in small plates which become yellow at 250° and melt and decompose at 287—290°; it dissolves slightly in alcohol, and to a less extent in water, yielding an acid solution; it behaves as a dibasic acid towards sodium hydroxide, and gives a white, insoluble, *silver* salt and coloured, insoluble *copper* and *ferrous* derivatives.

3 : 5-Dicyano-2 : 6-dioxy-4-methyl-4-ethylpiperidine, when neutralised with ammonia or sodium hydroxide, gives off a little ethane (see Grande, Abstr., 1898, i, 272); if magnesium hydroxide is used for the neutralisation, the amount of ethane obtained corresponds with the resolution of the piperidine derivative into dicyano-γ-methylglutaconimide and ethane.

3 : 5-*Dicyano*-2 : 6-*dioxy*-1 : 4-*dimethyl*-4-*ethylpiperidine*,

$C_5NH_2Me_2EtO_2(CN)_2$,

obtained from methyl ethyl ketone, ethyl cyanoacetate, and alcoholic methylamine, separates from dilute alcohol in sparkling laminæ or small crystals melting at 192·5°; it dissolves readily in pyridine, less so in alcohol or acetic acid, and slightly in water, forming an acid solution which, with ammonia and silver nitrate, yields a white precipitate; the aqueous solution gives a white precipitate with chlorine or bromine water, and when neutralised with ammonia decomposes into ethane and an unstable ammonium derivative of dicyano-1 : 4-dimethylglutaconimide which is immediately resolved into ammonia and dicyano-1 : 4-dimethylglutaconimide. The *dibromo*-derivative, $C_{11}H_{11}O_2N_3Br_2$, separates from dilute acetic acid in hard, prismatic, colourless crystals melting at 106—107·5° and when heated with acetic acid yields

3 : 5-*Dicyano*-1 : 4-*dimethyl*-4-*ethyltrimethylenedicarbonimide*,

$C_5NMe_2EtO_2(CN)_2$,

which crystallises from dilute alcohol in colourless needles melting at 161—162° and subliming in the form of very slender needles; it is soluble in alcohol or acetic acid and slightly so in water, giving a neutral solution, and it does not combine with bromine.

3 : 5-*Dicyano*-2 : 6-*dioxy*-4-*methyl*-1 : 4-*diethylpiperidine*,

$C_5NH_2MeEt_2O_2(CN)_2$,

prepared by the interaction of methyl ethyl ketone, ethyl cyanoacetate, and alcoholic ethylamine, crystallises from dilute alcohol in colourless laminæ which melt at 146—147·5° and dissolve slightly in water, giving an acid solution; on neutralising the latter with ammonia, ethane is evolved. The *dibromo*-derivative separates from dilute acetic acid in colourless crystals melting at 112—115°, and when heated with 50 per cent. acetic acid yields

3 : 5-*Dicyano*-4-*methyl*-1 : 4-*diethyltrimethylenedicarbonimide*,

$C_5NMeEt_2O_2(CN)_2$,

which crystallises from dilute acetic acid in light needles melting at 155·5°; it is soluble in pyridine or alcohol.

3 : 5-*Dicyano*-2 : 6-*dioxy*-4-*methyl*-4-*ethyl*-1-*allylpiperidine*,

$C_3H_5\cdot C_5NH_2MeEtO_2(CN)_2$,

prepared from methyl ethyl ketone, ethyl cyanoacetate, and alcoholic allylamine, crystallises from dilute alcohol in long, sparkling needles which melt at 91—92° and dissolve slightly in water, giving an acid solution.

3 : 5-*Dicyano*-2 : 6-*dioxy*-1 : 4-*dimethyl*-4-*propylpiperidine*,

$C_5NH_2Me_2Pr^aO_2(CN)_2$,

obtained from methyl propyl ketone, ethyl cyanoacetate, and alcoholic methylamine, crystallises from water in sparkling laminæ which melt at 134—135·5° and dissolve in alcohol, and to a less extent in water, yielding a strongly acid solution; it is soluble in alkali solution, and in presence of ammonia and mercury decomposes with evolution of propane.

3 : 5-*Dicyano*-2 : 6-*dioxy*-4-*methyl*-4-iso*propylpiperidine*,

$$C_5NH_3MePr^{\beta}O_2(CN)_2,$$

prepared from methyl *iso*propyl ketone, ethyl cyanoacetate, and ammonia, crystallises in plates melting at 232—234°; when neutralised with ammonia, propane is evolved. The *dibromo*-derivative, $C_{11}H_{11}O_2N_3Br_2$, melts at 163—165°.

3 : 5-*Dicyano*-4-*methyl*-4-iso*propyltrimethylenedicarbonimide*,

$$C_5NHMePr^{\beta}O_2(CN)_2,$$

has an acid reaction, and crystallises in prisms melting at about 240°.

[With Carlo Mensio.—3 : 5-*Dicyano*-2 : 6-*dioxy*-4-*methyl*-4-*butylpiperidine*, $C_4H_9 \cdot C_5NH_3MeO_2(CN)_2$, prepared from methyl butyl ketone, ethyl cyanoacetate, and alcoholic ammonia, separates from water in broad, nacreous plates which melt at 180—182° and dissolve readily in acetone, pyridine, or alkali solutions; on treating the aqueous solution with ammonia or magnesium hydroxide, butane is evolved. The *silver* salt, $C_{12}H_{14}O_2N_3Ag$, was prepared, and the *dibromo*-derivative, $C_{12}H_{13}O_2N_3Br_2$, which forms colourless crystals melting at 128—129° and is soluble in acetic acid. When heated with 50 per cent. acetic acid, the dibromo-compound yields

3 : 5-*Dicyano*-4-*methyl*-4-*butyltrimethylenedicarbonimide*,

$$C_4H_9 \cdot C_5NHMeO_2(CN)_2,$$

which forms white plates soluble in water and melting at 188—189°; when heated with dilute sodium hydroxide solution, it yields ammonia and the sodium salt of methylbutyldicyanotrimethylenedicarboxylic acid; the *silver* salt of the imide was prepared.

3 : 5-*Dicyano*-2 : 6-*dioxy*-1 : 4-*dimethyl*-4-*butylpiperidine*,

$$C_4H_9 \cdot C_5NH_2Me_2O_2(CN)_2,$$

prepared from methyl butyl ketone, ethyl cyanoacetate, and alcoholic methylamine, crystallises from dilute alcohol in colourless prisms melting at 123° and, when neutralised with ammonia, yields butane.

3 : 5-*Dicyano*-2 : 6-*dioxy*-4-*methyl*-4-iso*butylpiperidine*,

$$C_5NH_3MeO_2(CN)_2 \cdot CH_2 \cdot CHMe_2,$$

crystallises from dilute alcohol in long needles melting at 241—242° and is soluble in alkaline hydroxide or carbonate solution, or in alcohol, and to a slight extent in water, giving an acid solution; it decolorises bromine, and when neutralised with ammonia or magnesium hydroxide yields butane.

[With Silvio Baldi.—3 : 5-*Dicyano*-2 : 6-*dioxy*-4-*methyl*-4-iso*hexylpiperidine*, $C_5NH_3MeO_2(CN)_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CHMe_2$, prepared from methyl *iso*hexyl ketone, ethyl cyanoacetate, and alcoholic ammonia, crystallises from alcohol in sparkling laminæ melting at 166·5—168·5°; it is almost insoluble in water, has an acid reaction, and forms a *dibromo*-derivative.]

3 : 5-*Dicyano*-2 : 6-*dioxy*-4-*methyl* 4-iso*hexenylpiperidine*,

$$C_5NH_3MeO_2(CN)_2 \cdot CH_2 \cdot CH_2 \cdot CH:CMe_2,$$

prepared from methyl heptenone, ethyl cyanoacetate, and alcoholic ammonia, crystallises from alcohol in shining laminæ melting at 183—184·5°; it is soluble in alcohol, acetone, pyridine, or acetic acid, and slightly so in water, giving an acid solution.

3 : 5-*Dicyano*-2 : 6-*dioxy*-4-*methyl*-4-*nonylpiperidine*,
$C_5NH_3MeO_2(CN)_2\cdot CH_2\cdot[CH_2]_7\cdot CH_3$,
crystallises from alcohol in nacreous plates which melt at 136·5—137·5° and are greasy to the touch; it is soluble in alcohol or acetic acid and in potassium hydroxide or ammonia solution. The *ammonium* salt decomposes with evolution of nonane; the *silver*, *copper*, *calcium*, and *barium* salts and the *dibromo*-derivative were prepared.

3 : 5-*Dicyano*-2 : 6-*dioxy*-4-*ethyl*-4-*propylpiperidine*,
$C_5NH_3EtPr^aO_2(CN)_2$,
crystallises from dilute alcohol in sparkling plates melting at 216—217°; it is very soluble in pyridine and slightly so in water, yielding an acid solution which gives a white precipitate with aqueous chlorine or bromine; with potassium permanganate, it yields hydrogen cyanide, and the aqueous solution neutralised with ammonia does not evolve propane but ethane, the corresponding ammonium derivative of propyldicyanoglutaconimide being also formed; the *silver* and *cuprammonium* salts of this latter compound were also prepared. The *dibromo*-derivative of the dioxypiperidine, $C_{12}H_{13}O_2N_3Br_2$, separates from dilute acetic acid in colourless prisms melting at 159—161°, and when heated with acetic acid is converted into

3 : 5-*Dicyano*-4-*ethyl*-4-*propyltrimethylenedicarbonimide*,
$C_5NHEtPr^aO_2(CN)_2$,
crystallising in sparkling needles which melt at 186—186·5° and are soluble in alcohol.

3 : 5-*Dicyano*-2 : 6-*dioxy*-4 : 4-*dipropylpiperidine*, $C_5NH_3Pr^a{}_2O_2(CN)_2$, prepared from dipropyl ketone, ethyl cyanoacetate and alcoholic ammonia, separates from dilute alcohol either in long, silky needles or in heavy, prismatic crystals melting at 220·5°; it dissolves very readily in pyridine, less so in dilute potassium hydroxide or ammonia solution; in aqueous solution, it is decomposed by magnesium hydroxide and very rapidly by ammonia solution with evolution of propane, whilst calcium hydroxide is without action. Its *dibromo*-derivative separates from dilute acetic acid in dense, rhombic plates which melt at 136—138° and are soluble in acetic acid.

3 : 5-*Dicyano*-2 : 6-*dioxy*-4-*phenyl*-4-*methylpiperidine*,
$C_5NH_3MePhO_2(CN)_2$,
prepared from acetophenone, ethyl cyanoacetate, and alcoholic ammonia, separates from alcohol in nacreous laminæ which become brown at about 270° and melt at about 280°; it dissolves slightly in water and on neutralisation with alkalis behaves as a monobasic acid.

3 : 5-*Dicyano*-2 : 6-*dioxy*-4-*phenethyl*-4-*methylpiperidine*,
$C_5NH_3MeO_2(CN)_2\cdot CH_2\cdot CH_2Ph$,
crystallises from alcohol in shining, colourless, rhombic plates with blunted angles and melts at 223—224·5° to a reddish-brown liquid; when partially neutralised with dilute ammonia solution, it gradually decomposes into ethylbenzene and the ammonium salt of dicyanomethylglutaconimide; towards alkalis, it behaves like a dibasic acid. It forms white, crystalline *ammonium* and *magnesium* salts, a yellow, insoluble *copper* salt, and a white, sparingly soluble *silver* salt. The *dibromo*-derivative, $C_{16}H_{13}O_2N_3Br_2$, separates from dilute acetic acid

in blunt-angled, shining rhombs melting at 163—165°, and when heated with 50 per cent. acetic acid yields

3 : 5-*Dicyano-4-phenethyl-4-methyltrimethylenedicarbonimide*,

$$C_5NHMeO_2(CN)_2\cdot CH_2\cdot CH_2Ph,$$

which separates from dilute acetic acid in dense, colourless crystals melting at 203—205°; it dissolves sparingly in water, giving an acid solution, and when mixed with dilute sodium hydroxide solution and distilled in a current of steam it yields ammonia and 1 : 2-dicyano-3-methyl-3-phenethyltrimethylene-1 : 2-dicarboxylic acid.

3 : 5-*Dicyano*-2 : 6-*dioxy-4-phenethyl*-1 : 4-*dimethylpiperidine*,

$$C_5NH_2Me_2O_2(CN)_2\cdot CH_2\cdot CH_2Ph,$$

crystallises from alcohol in needles melting at 203—204°; it is slightly soluble in water, more so in acetic acid or alkali solution, and behaves as a monobasic acid.

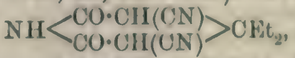
3 : 5-*Dicyano*-2 : 6-*dioxy-4-styryl-4-methylpiperidine*,

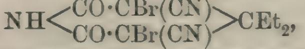
$$C_5NH_3MeO_2(CN)_2\cdot CH\colon CHPh,$$

obtained from benzylideneacetone, ethyl cyanoacetate, and alcoholic ammonia, melts at 275—277°, and on treating with ammonia and acidifying with hydrochloric acid, yields a *compound* separating in the form of short prisms or rhombic plates, melting and decomposing with evolution of gas at 281—283°; this compound is being further investigated.

From the results obtained in the preparation of the compounds above described, the following conclusions are drawn. Ketones containing normal chains react most readily with ethyl cyanoacetate and ammonia, or an amine, to form dicyanodioxypiperidine derivatives. The prolongation of one of the normal alkyl groups of the ketone increases the amount of product obtained, a result which is also produced by the presence of phenyl in one of the alkyl radicles. When the two radicles of the ketone are identical, the amount of product obtained decreases as the radicle increases in size. *iso*Ketones containing a CH_2 group, give good results, but with those in which a secondary, or tertiary, carbon atom is united directly with the carbonyl group, the reaction takes place with difficulty. With aromatic ketones having a phenyl radicle in direct combination with the carbonyl group, the reaction proceeds either with difficulty or not at all, but the opposite is the case if one or more CH_2 groups intervene between the phenyl and carbonyl radicles. In the decomposition of the ammonium or magnesium compounds of the dicyanodioxypiperidine derivatives prepared from ketones of the form $CH_3\cdot CO\cdot R$, methane is never evolved, but always a hydrocarbon of higher molecular weight. Other theoretical considerations, such as the influence of the large number of electronegative groups present in the molecules of these compounds on their acid character, are discussed. The author is continuing his researches.

T. H. P.

Derivatives of Diethyl Ketone. By EDOARDO PEANO (*Atti Accad. Sci. Torino*, 1900—1901, **36**, 187—195).—3 : 5-*Dicyano*-2 : 6-*dioxy*-4 : 4-*diethylpiperidine*,  $NH{<}{\begin{matrix}CO\cdot CH(CN)\\CO\cdot CH(CN)\end{matrix}}{>}CEt_2$, obtained together with cyanacetamide by the interaction of diethyl ketone, ethyl cyanoacetate, and alcoholic ammonia, forms thin, colourless, shining leaflets which melt at 200°, and dissolve slightly in water and to a greater extent in alcohol. The *silver* salt, $C_{11}H_{12}O_2N_3Ag$, is a white precipitate, and the *cuprammonium* salt, $(C_{11}H_{12}O_2N_3)_2Cu,4NH_3,H_2O$, forms bluish-violet crystals. On neutralising the aqueous solution with ammonia or magnesium hydroxide, it decomposes into ethane, and the ammonium salt of 3 : 5-dicyano-4-ethylglutaconimide already obtained by Treves (*Atti Accad. Sci. Torino*, 1899, **34**) by the action of ethyl cyanoacetate on propaldehyde in presence of ammonia. The *dibromo*-derivative of the dicyanodioxydiethylpiperidine,

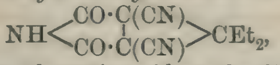


$$NH\left<\begin{array}{l}CO\cdot CBr(CN)\\CO\cdot CBr(CN)\end{array}\right>CEt_2,$$

crystallises from dilute acetic acid in short prisms, melting and decomposing at 182°.

By distillation with sodium hydroxide solution, the piperidine compound is decomposed into ammonia and sodium 1 : 2-dicyano-3 : 3-diethyltrimethylene-1 : 2-dicarboxylate.

3 : 5-*Dicyano*-4 : 4-*diethyltrimethylenedicarbonimide*,



$$NH\left<\begin{array}{l}CO\cdot C(CN)\\ \quad\;\, |\\CO\cdot C(CN)\end{array}\right>CEt_2,$$

obtained by the action of acetic acid on the dibromo-compound above described, melts at 202° and forms a *silver* salt obtained as a white precipitate. T. H. P.

Action of Nitric Acid on Tetriodopyrrole (Iodole). By H. Cousin (*J. Pharm.*, 1901, [vi], **13**, 269—272).—When tetriodopyrrole in ethereal solution is treated in the cold with a mixture of nitric and acetic acids, it yields two nitro-compounds, of which the more abundant *nitrotriiodopyrrole*, $C_4NHI_3\cdot NO_2$, crystallising in stellate groups of golden-yellow, prismatic needles, can be separated from the second by its much greater solubility in absolute alcohol. It is very sparingly soluble in hot water, benzene, or chloroform, but copiously in ether, and decomposes at 185—187° without fusion; the hydrogen atom is replaceable by metals, with formation of reddish-orange, explosive salts. The second compound is reserved for future investigation.

Dinitrodiiodopyrrole, $C_4NHI_2(NO_2)_2$, formed by the action of fuming nitric acid at 100° on the preceding compound, forms golden-yellow, crystalline plates, sparingly soluble in cold water, readily so in alcohol, melts and decomposes at 190—192°, and forms reddish-orange alkali salts, that of potassium being sparingly soluble in cold water.

M. J. S.

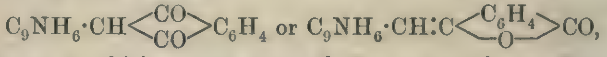
Studies on Isatin. By Leon Marchlewski and J. Buraczewski (*Bull. Acad. Sci. Cracow*, 1900, 374—376. Compare Abstr., 1900, i, 100).—The condensation of acetyl-ψ-isatin with *o*-phenylenediamine produces *o*-aminophenylhydroxyquinoxaline, and not *o*-aminophenimesatine (*loc. cit.*). For both indophenazine and a quinoxaline derivative to be formed from isatin and *o*-phenylenediamine in aqueous solution, the isatin must either be present as isatinic acid or as a mixture of lactim and lactam.

o-Acetylaminophenylhydroxyquinoxaline, *o-nitrophenylhydroxyethoxy-*

quinoxaline, and o-*acetylaminophenylhydroxymethylquinoxaline*, have been prepared.

The products of alkylation of indophenazine are identical with the condensation products of alkyl-ψ-isatins with *o*-phenylenediamine, but the condensation of alkylated *o*-diamines with isatin leads to the formation of isomerides of the alkyl-indophenazines; these are called by the author alkyl-ψ-indophenazines. Of the indophenazine series, a *carboxylic acid*, and two isomeric *ethoxyindophenazines* have been prepared. Methyl-ψ-isatin and semicarbazide react, yielding two isomerides of the formula $C_{10}H_{10}O_2N_4$. K. J. P. O.

Constitution of Quinophthalone and the Two Isomeric Quinophthalines. By Alexander Eibner and O. Lange (*Annalen*, 1901, **315**, 303—356).—Quinophthalone, the base of quinoline-yellow, is produced by condensing quinaldine with phthalic anhydride; it may have the constitution,



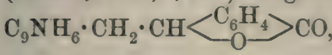
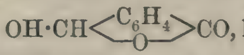
$$C_9NH_6{\cdot}CH\left\langle\begin{smallmatrix}CO\\CO\end{smallmatrix}\right\rangle C_6H_4 \text{ or } C_9NH_6{\cdot}CH{:}C\left\langle\begin{smallmatrix}C_6H_4\\O\end{smallmatrix}\right\rangle CO,$$

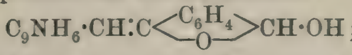
according as to which oxygen atom of the anhydride is eliminated in the condensation. The experimental results now obtained support the view that the colouring matter possesses the asymmetric constitution represented by the second of these formulæ.

On adding bromine to an acetic acid solution of quinophthalone, a mixture of bromo-derivatives is obtained. The *tribromo*-compound, $C_{18}H_{10}O_2NBr_3$, is precipitated from the acetic acid solution in orange-red needles which become yellow at 200° and melt at 228°; this substance when shaken with water yields the original base, and when treated with absolute alcohol gives rise to the *monobromo*-compound, $C_{18}H_{10}O_2NBr$, which is also produced by direct bromination; it crystallises in yellow needles, melts at 174°, and when boiled with alcohol or warmed for a short time with solutions of the alkali hydroxides or carbonates is reconverted into quinophthalone.

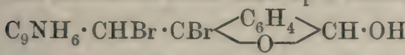
Dinitroquinophthalone, $C_{18}H_{11}O_6N_3$, produced by passing nitrogen tetroxide into a cooled glacial acetic acid solution of quinophthalone, is precipitated, on the addition of water, in white flakes; it melts indefinitely at about 133°. *Nitroquinophthalone*, $C_{18}H_{10}O_4N_2$, obtained by the action of the nitrous fumes from nitric acid and arsenious oxide on quinophthalone dissolved in acetic acid, crystallises in felted, yellow needles, and melts at 140°. It is also produced by boiling the preceding compound with alcohol, and is itself reconverted into the original colouring matter by the action of alkalis or dilute acids.

The ease with which quinophthalone is regenerated from its bromo- and nitro-derivatives indicates that the substances are of the nature of additive products, the formation of which depends on the existence, in its molecule, of a double linking corresponding with that indicated in the asymmetric formula. Phthalic chloride, which is represented as having an asymmetric constitution, condenses with quinaldine to form a *compound*, $C_9NH_6{\cdot}CH_2{\cdot}C(OH)\left\langle\begin{smallmatrix}C_6H_4\\O\end{smallmatrix}\right\rangle CO$, which crystallises in yellow needles, melts at 124°, and when heated, either alone or with sodium hydroxide solution, yields quinophthalone. This condensation product is also obtained as an intermediate step in the preparation of quinophthalone, providing that the temperature is maintained below 150°.

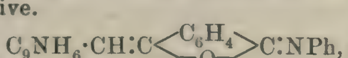
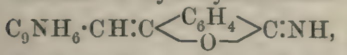
An almost quantitative yield of quinophthalone is obtained by heating on the water-bath a mixture of diethyl phthalate, quinaldine, and sodium wire; it is also readily produced by adding bromine to a benzene solution of phthalidylquinaldine (m. p. 104°), and heating the *dibromide*, $C_{18}H_{12}O_2NBr_2$, until the evolution of hydrogen bromide ceases. Nencki (Abstr., 1896, i, 256) assigned to phthalidylquinaldine the constitution  $C_9NH_6\cdot CH_2\cdot CH\left<\begin{matrix}C_6H_4\\O\end{matrix}\right>CO$, supposing that the hydroxyl group of phthalaldehydic acid,  $OH\cdot CH\left<\begin{matrix}C_6H_4\\O\end{matrix}\right>CO$, had been eliminated in the condensation; the preceding results are, however, more readily explained on the assumption that the carbonyl group is involved in the condensation, and that the product has the constitution

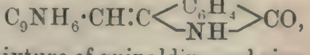


$$C_9NH_6\cdot CH\!:\!C\left<\begin{matrix}C_6H_4\\O\end{matrix}\right>CH\cdot OH;$$

this substance could take up 2 atoms of bromine to form a dibromide,  $C_9NH_6\cdot CHBr\cdot CBr\left<\begin{matrix}C_6H_4\\O\end{matrix}\right>CH\cdot OH$, from which quinophthalone would be obtained by the subsequent elimination of hydrogen bromide. The dibromide is quite stable in boiling benzene, and crystallises from this solvent in colourless leaflets melting at 108°.

Quinophthalone forms unstable alkali derivatives when treated with alcoholic solutions of the alkali hydroxides, but is not decomposed on heating at 200° with excess of sodium methoxide or the corresponding ethyl or amyl derivative.

Quinophthaloneanil,  $C_9NH_6\cdot CH\!:\!C\left<\begin{matrix}C_6H_4\\O\end{matrix}\right>C\!:\!NPh$, produced by heating together a mixture of aniline, zinc chloride, and the colouring matter, crystallises from alcohol or chloroform in red, felted needles and melts at 232°; it is also readily obtained by condensing its generators in a benzene solution in the presence of aluminium chloride. The anil is hydrolysed either by acid or alkalis. α-Quinophthaline,  $C_9NH_6\cdot CH\!:\!C\left<\begin{matrix}C_6H_4\\O\end{matrix}\right>C\!:\!NH$, produced by heating quinophthalone with alcoholic ammonia at 200°, melts at 305°, and yields a *platinichloride* and a *bromo*-derivative, $C_{18}H_{11}ON_2Br$, melting respectively at 278° and 100°; it is readily decomposed by aniline or phenylhydrazine, the former base giving rise to quinophthaloneanil whilst the latter furnishes a *compound*, $C_{24}H_{17}ON_3$, crystallising in red, felted needles and melting at 165°. α-Quinophthaline is readily hydrolysed to quinophthalone by mineral acids and also when heated to 200° with methyl alcohol. These reactions indicate that the base is an imino-derivative of quinophthalone, the imino-group being, in fact, eliminated in the form of ammonia in the foregoing decompositions.

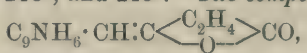
An isomeric base, *β-quinophthaline*,  $C_9NH_6\cdot CH\!:\!C\left<\begin{matrix}C_6H_4\\NH\end{matrix}\right>CO$, produced by slowly adding phthalimide to a mixture of quinaldine and zinc chloride heated at 160—180°, separates in the form of its *sulphate*,

$$C_{18}H_{12}ON_2,H_2SO_4,$$

on dissolving the fused mass in concentrated sulphuric acid and pouring the solution into water. The base separates from acetic acid or alcohol in yellow, cubic crystals and melts at 213°; it is less basic than its isomeride and dissolves more readily in the organic solvents. Its salts are yellow and amorphous, it forms a *silver* derivative, $C_{18}H_{11}ON_2Ag$, but does not interact with the alkali hydroxides, phenylhydrazine, acetic anhydride or benzoic chloride. Unlike its α-isomeride, it is not easily converted into quinophthalone on heating with mineral acids, the action only taking place in sealed tubes at temperatures above 100°. The base, when treated with bromine in glacial acetic acid solution, yields a mixture of *mono-* and *tri-bromo*-derivatives melting respectively at 56—59° and 170°; the monobromo-compound, when boiled with alcohol or warmed with alkaline solutions, is reconverted into the original substance.

β-Quinophthaline and aniline do not react even at boiling point of the latter base, but on adding zinc chloride to the mixture ammonia is eliminated, and quinaldine and phthalanil are produced.

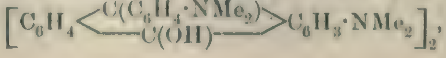
Succinimidequinaldine, $C_9NH_6\cdot CH{:}C<\begin{matrix}C_2H_4\\NH\end{matrix}>CO$, prepared by heating together succinimide, quinaldine, and zinc chloride, dissolving the product in concentrated sulphuric acid, adding the solution to water, and decomposing the precipitated sulphate by ammonia, crystallises from alcohol in feathery aggregates of leaflets and melts at 128°; it sublimes at higher temperatures and decomposes at 220°. Its solution in neutral solvents exhibits an intense green fluorescence which is diminished by the addition of acids; the substance separates from benzene in thick, lemon-yellow crystals having a violet reflex. The *hydrochloride* crystallises in yellow needles, the sulphate and the *platinichoride*, $C_{14}H_{12}ON_2,H_2PtCl_6$, in yellow prisms, these salts melt respectively at 240°, 218°, and 215°. The *compound*



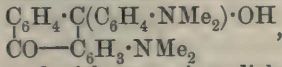
$$C_9NH_6\cdot CH{:}C<\begin{matrix}C_2H_4\\O\end{matrix}>CO,$$

analogous to quinophthalone, could not be obtained by the direct condensation of quinaldine and succinic anhydride; it was, however, prepared by heating the preceding base with hydrochloric acid at 100°. The product crystallises from alcohol in aggregates of brilliant yellow needles, and melts at 108°. G. T. M.

Tetramethyldiaminophenylanthranol and Tetramethyldiaminophenyloxanthranol. By ALBIN HALLER and ALFRED GUYOT (*Bull. Soc. Chim.*, 1901, [iii], **25**, 315—322).—Dimethylaminobenzoylbenzoic acid condenses with dimethylaniline in the presence of acetic anhydride to form dimethylanilinophthalein, $CO<\begin{matrix}O\\C_6H_4\end{matrix}>C(C_6H_4\cdot NMe_2)_2$, which is reduced by zinc in hydrochloric acid solution to dimethylanilinophthalin or tetramethyldiaminotriphenylmethane-*o*-carboxylic acid, $CO_2H\cdot C_6H_4\cdot CH(C_6H_4\cdot NMe_2)_2$. The latter compound, when dissolved in dimethylaniline and treated with phosphorus oxychloride, condenses to *bistetramethyldiaminophenylanthranol*,



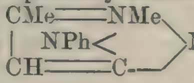
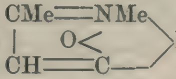
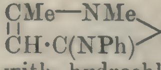
$$\left[C_6H_4<\begin{matrix}C(C_6H_4\cdot NMe_2)\\C(OH)\end{matrix}>C_6H_3\cdot NMe_2\right]_2,$$

which crystallises from boiling toluene in large scales containing 1 mol. of the solvent; when heated to 200°, it becomes phosphorescent through oxidation, and melts at about 275°. *Tetramethyldiaminophenyloxanthranol*,  $\begin{array}{l} C_6H_4\cdot C(C_6H_4\cdot NMe_2)\cdot OH \\ CO—C_6H_3\cdot NMe_2 \end{array}$, obtained by oxidising the preceding compound with potassium dichromate or ferric chloride, crystallises from chloroform in large, pale-yellow prisms melting at 213°, dissolves in sulphuric acid with the red coloration characteristic of phenyloxanthranols, and differs entirely from the substance described under the same name by O. Fischer (*Annalen*, 1881, **206**, 112). In the oxidation of the anthranol, a fugitive blue coloration is observed, which is due to the formation of an unstable *salt*, which subsequently undergoes hydrolysis; it forms, with zinc chloride, a rather more stable *compound*, crystallising in small, bronze coloured needles.

N. L.

The Law of Auxochromes. By PAUL LEMOULT (*Compt. rend.*, 1901, **132**, 784—787).—The author contends, in reply to Camichel and Bayrac (this vol., i, 296) that the law of auxochromes holds good for triphenylmethane derivatives containing 2 atoms of tertiary nitrogen, as in tetramethyldiaminotriphenylcarbinol oxalate and tetraethyldiaminotriphenylcarbinol sulphate, or 3 atoms of tertiary nitrogen as in hexaethyltriaminotriphenylcarbinol hydrochloride, and sodium dimethyldiethyldibenzyltriaminotriphenylcarbinoldisulphonate. Diagrams of the spectra are given, showing that the maximum of the unabsorbed red band is the same for both members of each of these pairs of compounds, but differs in the case of the two pairs. Care is required to determine the exact position of maximum transparence and the selection of a suitable degree of dilution of the solution is important.

C. H. B.

Action of Aniline and of Ammonia on 5-Chloro-1-phenyl-3-methylpyrazole Methochloride. By AUGUST MICHAELIS and E. GUNKEL (*Ber.*, 1901, **34**, 723—727).—The compound formed by heating aniline with antipyrine and phosphorus oxychloride (Silberstein, German Patent, 1899, 113384) probably owes its origin to the intermediate formation of 5-chloro-1-phenyl-3-methylpyrazole methochloride (Abstr., 1899, i, 941), as it is obtained when the latter is heated with aniline for 8 hours at 250°; it probably therefore is an *aniloantipyrine* (*anilopyrine*) of the formula,  $\begin{array}{l} CMe{=}NMe \\ |\quad NPh< \quad >NPh \\ CH{=}C— \end{array}$, corresponding with the formula  $\begin{array}{l} CMe{=}NMe \\ |\quad O< \quad >NPh \\ CH{=}C— \end{array}$ for antipyrine. This constitution is more probable than  $\begin{array}{l} CMe—NMe \\ \| \qquad\quad >NPh \\ CH\cdot C(NPh) \end{array}$, as the substance is not changed when heated with hydrochloric acid at 150° or with alcoholic potassium hydroxide, whereas benzylideneaniline, CHPh:NPh, and similar compounds always lose aniline when similarly treated.

With excess of nitric acid, anilopyrine yields two *compounds*, *one* almost insoluble in alcohol, and the *other* easily soluble. The former crystallises from glacial acetic acid in red needles, and has the composition $C_{12}H_8N_3\cdot NO_2$, as it yields on reduction with tin and hydrochloric acid an *amino*-compound, $C_{12}H_8N_3\cdot NH_2$, which crystallises from alcohol in small, dark-red, lustrous leaflets and melts at 215°; the latter forms citron-yellow leaflets, melts at 164°, and probably also contains a nitro-group.

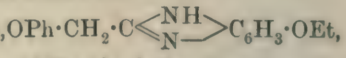
Anilopyrine combines with methyl iodide at 100° to form the *compound*, $C_{17}H_{17}N_3,MeI$, which crystallises from water in yellowish prisms and melts at 174°.

Aqueous or alcoholic ammonia does not act on antipyrine chloride (5-chloro-1-phenyl-3-methylpyrazole methochloride) at a high temperature, but ammonium carbonate after 12 hours at 200° yields *iminopyrine*, $C_{11}H_{12}N_2{:}NH$, which crystallises from toluene in white needles and melts at 116°. W. A. D.

Acetylenic Ketones. Synthesis of β-Diketones. By CHARLES MOUREU and RAYMOND DELANGE (*Bull. Soc. Chim.*, 1901, [iii], **25**, 302—313).—Mainly an account of work already published (Abstr., 1900, i, 397; this vol., i, 14. Compare also Nef, Abstr., 1900, i, 20). The action of semicarbazide on benzoylheptinene results in the formation of hydrazodicarbonamide and *3-phenyl-5-amylpyrazole*, which crystallises from light petroleum in slightly yellow prisms melting at 76°. This substance is also produced by the action of hydrazine sulphate on benzoylheptinene. N. L.

Aromatic Phenoxyacetamidines. By GEORG COHN (*J. pr. Chem.*, 1901, [ii], **63**, 188—192).—By the condensation of phenoxyacetic acid and some of its derivatives with the *o*-diamines, 3 : 4-diaminophenetole or 3 : 4-tolylenediamine, the following phenoxyacetamidines have been obtained, the condensation being brought about by heating mixtures of the acid and base at about 150°.

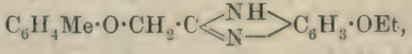
2-*Phenoxymethyl*-6-*ethoxybenziminazole*,



$OPh\cdot CH_2\cdot C{<}\substack{NH\\ N}{>}C_6H_3\cdot OEt$,

forms colourless plates melting at 168—169°; the *hydrochloride* melts at 205°, and the *picrate*, which forms thin plates, at 211—212°.

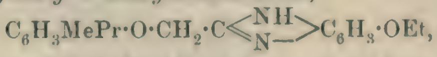
2-p-*Tolyloxymethyl*-5-*ethoxybenziminazole*,



$C_6H_4Me\cdot O\cdot CH_2\cdot C{<}\substack{NH\\ N}{>}C_6H_3\cdot OEt$,

crystallises in colourless plates melting at 145—146°; the *picrate* forms a crystalline precipitate melting at 226—227°.

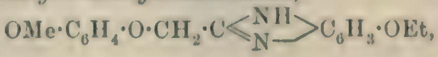
2-m-*Thymoxymethyl*-5-*ethoxybenziminazole*,



$C_6H_3MePr\cdot O\cdot CH_2\cdot C{<}\substack{NH\\ N}{>}C_6H_3\cdot OEt$,

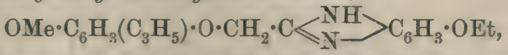
melts at 84—86°; the *hydrochloride* forms plates from alcohol melting at 208°; the *picrate* melts at 194°. The isomeric *carvacrol* derivative melts at 124—125°; the *picrate* crystallises in greenish-yellow plates melting at 204°.

2-*Guaiacoxymethyl*-5-*ethoxybenziminazole*,



$OMe\cdot C_6H_4\cdot O\cdot CH_2\cdot C{<}\substack{NH\\ N}{>}C_6H_3\cdot OEt$, crystallises in faintly violet needles melting at 122—123°; the *picrate* forms large, greenish needles which melt at 174°.

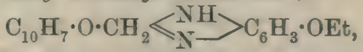
2-m-*Eugenoxymethyl*-5-*ethoxybenziminazole*,



$$\mathrm{OMe\cdot C_6H_3(C_3H_5)\cdot O\cdot CH_2\cdot C}{<}\genfrac{}{}{0pt}{}{\mathrm{NH}}{\mathrm{N}}{>}\mathrm{C_6H_3\cdot OEt},$$

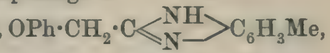
forms needles melting at 75—76°; the *hydrochloride* forms greenish needles, and the *picrate* needles melting at 125°.

2-α-*Naphthyloxymethyl*-5-*ethoxybenziminazole*,



$$\mathrm{C_{10}H_7\cdot O\cdot CH_2}{<}\genfrac{}{}{0pt}{}{\mathrm{NH}}{\mathrm{N}}{>}\mathrm{C_6H_3\cdot OEt},$$

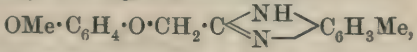
melts at 190°, and forms a *picrate* melting at 227—228°. The *β-naphthyl* derivative melts at 163—165°, the *hydrochloride* at 221°, and the *picrate* at 249—250°, both decomposing.

2-*Phenoxymethyl*-5-*methylbenziminazole*, 

$$\mathrm{OPh\cdot CH_2\cdot C}{<}\genfrac{}{}{0pt}{}{\mathrm{NH}}{\mathrm{N}}{>}\mathrm{C_6H_3Me},$$

melts at 170—171°; the *picrate* forms yellow needles melting at 216—217°.

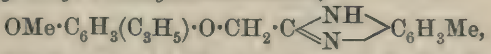
2-*Guaiacoxymethyl*-5-*methylbenziminazole*,



$$\mathrm{OMe\cdot C_6H_4\cdot O\cdot CH_2\cdot C}{<}\genfrac{}{}{0pt}{}{\mathrm{NH}}{\mathrm{N}}{>}\mathrm{C_6H_3Me},$$

forms star-shaped aggregates of needles melting at 78—80°; the *picrate* melts at 179°.

2-*Eugenoxymethyl*-5-*methylbenziminazole*,



$$\mathrm{OMe\cdot C_6H_3(C_3H_5)\cdot O\cdot CH_2\cdot C}{<}\genfrac{}{}{0pt}{}{\mathrm{NH}}{\mathrm{N}}{>}\mathrm{C_6H_3Me},$$

forms lustrous plates melting at 71—73°; the *picrate* melts at 132°.

K. J. P. O.

Condensation of Glyoxal and Benzaldehyde with Ammonia. By L. Wewiórski (*Bull. Acad. Sci. Cracow*, 1900, 398—399).—By the action of ammonia on a dilute aqueous solution of glyoxal and benzaldehyde, a 60 per cent. yield of 2-phenylglyoxaline is obtained. When ammonia gas is employed, and alcohol used as the solvent, hydrobenzamide, glyoxaline, glycosine, and much tarry substance are formed.

2-*Phenylglyoxaline* crystallises in white scales or needles melting at 148°; the *hydrochloride* forms long, white needles melting at 67·5—68°; the *sulphate* melts at 186—187°; the *platinichloride* forms orange-yellow needles. 2-*Phenyl*-1-*methylglyoxaline* and 2-*phenyl*-1-*ethylglyoxaline* are oily liquids; the latter boils at 300—305°, and has a sp. gr. 1·0522 at 18°, and a molecular refraction 54·49.

K. J. P. O.

Chemistry of Elastic Ligament. By A. N. Richards and William J. Gies (*Proc. Amer. Physiol. Soc.*, 1900, xi—xii; *Amer. J. Physiol.*, 5).—Ligamentum nuchæ of the ox contains appreciable quantities of mucin, having all the characters of the glucoproteid separable from white fibrous tissue. Like coagulable proteids, it is easily removed by extraction for a few days with lime-water. This renders subsequent extraction with hot alkali unnecessary. Elastin prepared after such extraction contains less sulphur (0·13 to 0·17 per cent.) than that prepared by older methods. The distribution of nitrogen by Schultze's method is 1·73 as ammonia, 3·08 as bases, and 95·23 as amino-acids. W. D. H.

Chemical Nature of the Tetanus Poison, and the Chemistry of Albumoses. By H. Hayashi (*Chem. Centr.*, 1901, i, 411—412; from *Comm. Med. Fac. Imp. Jap. Univ., Tokio*, **4**, 341—362).—The precipitate formed by adding zinc chloride to a solution of Witte's peptone which has been treated with sodium carbonate solution is a double compound of basic zinc carbonate and albumoses, and contains at the most only traces of peptones. This "zinc carbonoalbumosate" in the moist state is soluble in ammonium sulphate solution and the albumoses are precipitated from the solution by saturating it with ammonium sulphate. The zinc compound of the tetanus poison (compare Brieger and Fraenkel, *Ber. klin. Woch.*, **27**, 241) is soluble in sodium hydroxide solution, and gives the biuret reaction (compare Brieger and Boer, *Zeit. Hyg.*, **21**, 259). The poisonous compound obtained from this substance, however, contains zinc. From the behaviour of the zinc compound, the author concludes that the tetanus poison may belong to the group of albumoses, or that it contains an albumose combined with the poisonous substance, or that the latter is only carried down mechanically. The zinc compound is decomposed by ammonium sulphate and contains peptones in a state of combination. When the tetanus culture is neutralised with magnesium carbonate instead of with sodium carbonate, zinc chloride does not precipitate the whole of the poison. E. W. W.

Antipeptone. By Fr. Kutscher (*Ber.*, 1901, **34**, 504—506).—A reply to Siegfried (this vol., i, 176). C. F. B.

Epinephrine. By John J. Abel (*Proc. Amer. Physiol. Soc.*, 1900, v—vi. Compare Abstr., 1899, i, 395; 1900, i, 72).—If the autoclave is not used in the preparation of epinephrine, a more active product is obtained. Von Fürth's suprarenine (Abstr., 1900, ii, 292) is only a modification of epinephrine, being the native principle not subjected to benzoating or treatment in the autoclave. W. D. H.

Nature of Melanins and Allied Substances. By V. Ducceschi (*Atti Real. Accad. Lincei*, 1901, [v], **10**, i, 180—188).—By the action of concentrated hydrochloric acid and potassium chlorate on tyrosine, a compound is obtained giving reactions identical with those of melanoidic acid prepared by Schmiedeberg by treating serum albumin with dilute hydrochloric acid (Abstr., 1898, i, 342).

When tyrosine is treated with concentrated hydrochloric acid and sodium nitrite, it yields a substance having all the reactions and properties given by von Fürth ("The Action of Nitric Acid on Proteids," Strassburg, 1899) as characteristic of the xanthomelanin obtained by the action of fuming nitric acid on casein or scrapings of horn.

The action of bromine on tyrosine in presence of water yields two substances, one soluble and the other insoluble in 95 per cent. alcohol; on fusion with potassium hydroxide, these give a distinct odour of indole or scatole, and in their method of preparation and isolation and in most of their reactions correspond with compounds (bromoproteinchrome) prepared by the action of bromine on the products of pancreatic digestion.

The small quantities of these products obtained have not allowed of their complete analysis, and the investigations are being continued.

T. H. P.

Products of Papain and Bromelin Proteolysis. By LAFAYETTE B. MENDEL and F. P. UNDERHILL (*Proc. Amer. Physiol. Soc.*, 1900, xiii—xiv).—Papain shows proteolytic activity in both alkaline and slightly acid media. The primary products correspond closely to those obtained from peptic digestions. Leucine, tyrosine, and tryptophan do not occur if bacteria are excluded. Bromelin, on the other hand, readily forms leucine, tyrosine, and tryptophan, even in acid media.

W. D. H.

Aromatic Boron Compounds. By AUGUST MICHAELIS (*Annalen*, 1901, **315**, 19—43. Compare Abstr., 1894, i, 190).—[With G. THEVÉNOT].—m-*Xylylborochloride*, $C_6H_3Me_2\cdot BCl_2$, prepared by heating *m*-mercurydixylyl with boron chloride at 200° during 24 hours, is a colourless liquid which fumes in air and boils at 218°. m-*Xylylboroxide*, $C_6H_3Me_2\cdot BO$, obtained on adding the chloride to water, forms white needles and melts at 202°. Boiling water converts the oxide into *m*-xylylboric acid, $C_6H_3Me_2\cdot B(OH)_2$, of which the *diethyl* salt boils at 160°; the *hydrogen silver* salt is pale yellow.

p-*Xylylborochloride* is a colourless liquid which boils at 205° and fumes in air. p-*Xylylboric acid* crystallises from hot water in aggregates of slender needles, and melts at 186°; the *oxide* melts at 176°.

o-*Xylylborochloride* melts at 0°, and boils at 212°. o-*Xylylboric acid* crystallises from water in colourless, slender needles, and melts at 190·5°; the *oxide* melts at 226°.

[With E. RICHTER.]—A study of the following compounds necessitated the preparation of boron bromide; details of this operation are included in the paper, which also contains an illustration of the apparatus employed.

Phenylborobromide, $BPhBr_2$, prepared by heating mercurydiphenyl with boron bromide and benzene in a reflux apparatus provided with a calcium chloride tube, crystallises in colourless plates, melts at 32—34°, and boils at 99—101° under 20 mm. pressure; the compound has a penetrating odour, and fumes on exposure to air. Water decomposes it vigorously, forming phenylboric acid. *Diphenylborobromide*, BPh_2Br, a bye-product in the preparation of the foregoing substance, forms a colourless, crystalline mass which rapidly becomes red in air; it melts at 24—25°, and boils at 150—160° under 8 mm. pressure. Water converts it into diphenylboric acid.

p-*Tolylborobromide*, $C_6H_4Me\cdot BBr_2$, melts at 44—45°, and boils at 145° under 25 mm. pressure; it fumes in air, and yields *p*-tolylboric acid under the influence of water. p-*Tolylboroxide*, $C_6H_4Me\cdot BO$, produced when p-tolylboric acid is exposed to a dry atmosphere, melts at 257—258°.

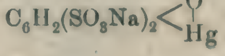
m-*Xylylborobromide*, $C_6H_3Me_2\cdot BBr_2$, is a colourless, refractive liquid which boils at 125° under 15 mm. pressure, and has a sp. gr. 1·57 at 15°.

ψ-Cumylborobromide, $C_6H_2Me_3\cdot BBr_2$, is a colourless liquid which boils at 170—190° under 16 mm. pressure, a portion undergoing decomposition in the process; water converts it into *ψ-cumylboroxide*, $C_6H_2Me_3\cdot BO$, which crystallises from ether in lustrous, white needles and melts at 211°.

p-*Borobenzoic acid*, $CO_2H\cdot C_6H_4\cdot B(OH)_2$, prepared by oxidising an alkaline solution of tolylboric acid with potassium permanganate, crystallises from hot water in lustrous, white, highly refractive needles which melt at 225°; it does not yield the anhydride when heated, merely volatilising at 125°, but when heated rapidly, the substance is resolved into benzoic acid, boric anhydride, and water. On treating a hot, aqueous solution of borobenzoic acid with mercuric chloride, *chloromercuribenzoic acid*, $HgCl\cdot C_6H_4\cdot CO_2H$, is produced, forming a white, crystalline powder which melts at 272°, and dissolves in absolute alcohol; it is insoluble in water, but dissolves in aqueous alkalis. The *barium* salt of *p*-borobenzoic acid contains $1H_2O$, and is more readily soluble in cold water than in hot; the *lead* and *silver* salts are amorphous.

Diphenylboric acid, $BPh_2\cdot OH$, is difficult to obtain in the purified state; it is a colourless liquid having a powerful smell, and boils at 215—235° under 17 mm. pressure. The *anhydride* of *p*-ditolylboric acid, $[(C_6H_4Me)_2B]_2O$, prepared by heating mercuryditolyl with boron bromide and benzene and treating the product with water, separates from the latter as a white, crystalline powder and melts at 78°.

[With F. Hillringhaus].—*Phenyl borate*, $B(OPh)_3$, prepared by heating phenol (3 mols.) with boron chloride and benzene in a sealed tube at 100° during 12 hours, is a colourless, crystalline substance; it melts very readily, and is resolved by water into phenol and boric acid. m-*Tolyl borate*, $B(O\cdot C_6H_4Me)_3$, melts at 40°, and *β-naphthyl borate*, $B(O\cdot C_{10}H_7)_3$, crystallises from benzene in colourless leaflets and melts at 115°. M. O. F.

Action of Mercuric Oxide on some Organic Substances. By Alphonse Lumière, Louis Lumière, and F. Perrin (*Compt. rend.*, 1901, 132, 635—637).—Compounds analogous to sodium mercuriphenoldisulphonate (this vol., i, 244) seem to be generally formed by substances containing phenolic hydroxyl, unless, like the aminophenols, they undergo oxidation. They are, however, not formed by compounds, such as anisole and phenetole, in which the hydrogen of the hydroxyl group is replaced, or by substances, like trinitrophenol and *s*-trichlorophenol, in which the ortho- and para-positions are occupied. Sodium mercuriguaiacolsulphonate has been prepared; its properties are similar to those of the corresponding phenol compound. The constitutions $Hg_2[O\cdot C_6H_3(SO_3Na)_2]_2$ or  $C_6H_2(SO_3Na)_2<\begin{array}{l}O\\ |\\ Hg\end{array}$ are suggested for the latter derivative. N. L.

Organic Chemistry.

Addition of Hydrogen and other Simple Molecules to Unsaturated Compounds. By EMIL ERLENMEYER, jun. (*Annalen*, 1901, **316**, 43—56).—A theoretical discussion as to the mode in which molecules of hydrogen and other elements and compounds combine with unsaturated carbon compounds (compare Thiele, Abstr., 1899, i, 554). G. T. M.

Intramolecular Migration and its Explanation based on the Intramolecular Mobility of Multivalent Elements. By EMIL ERLENMEYER, jun. (*Annalen*, 1901, **316**, 75—88).—A theoretical discussion not suitable for abstraction. G. T. M.

Heptane from Coniferous Trees. By W. C. BLASDALE (*J. Amer. Chem. Soc.*, 1901, **23**, 163—164).—Thorpe (Trans., 1879, **35**, 297) has shown that the substance obtained by distillation from the exudation of *Pinus Sabiniana* consists of *n*-heptane. The author has confirmed this, and has found that *n*-heptane is also furnished by the resinous secretion of *P. Jeffreyi*, whilst those of *P. Murrayana*, *Abies concolor* v. *Lowiana* and *Pseudotsuga taxifolia* yield terpenes similar to those obtained from other coniferous trees. E. G.

The Chemistry of Methylene. By VICTOR THOMAS (*Compt. rend.*, 1901, **132**, 1118—1121).—The compounds described by Sakurai (Trans., 1880, **37**, 658, and 1881, **39**, 485) as obtained by the action of mercury on methylene iodide are formed at the ordinary temperature even in complete absence of iodoform or mercurous iodide. If mercury is heated at 190—200° in sealed tubes with methylene iodide, a mixture of methane and ethane is obtained; if the methylene iodide is heated with silver at 100° to 150°, the gaseous products contain a considerable proportion of acetylene. It would seem that methylene, CH_2, splits up into CH and H, the former condensing to form acetylene, whilst the latter unites with undecomposed methylene to form methane and ethane. C. H. B.

Formation of Chloroform from Lactic Acid. By OTTO EBERHARD (*Zeit. öffentl. Chem.*, 1901, **7**, 125—126).—By the action of the calculated quantity of bleaching powder containing 23 per cent. of available chlorine, mixed with 10 times its weight of water, on lactic acid, chloroform is obtained. The equation $2[CH_3\cdot CH(OH)\cdot CO_2]_2Ca + 12CaOCl_2 = (CHO_2)_2Ca + 2CHCl_3 + 9CaCl_2 + 5H_2O + 3CaCO_3 + CO_2 + (C_2H_3O_2)_2Ca$ best represents the quantities of chloroform and formic acid produced. With bleaching powder above 25 per cent. strength, the yield of chloroform becomes less. K. J. P. O.

Action of Acid Chlorides on Ethers in Presence of Zinc Chloride. By MARCEL DESCUDÉ (*Compt. rend.*, 1901, **132**, 1129—1131).—When ethyl ether is heated with acetyl chloride in presence of zinc chloride, ethyl chloride is obtained in quantity corresponding with the equation $CH_3{\cdot}COCl + Et_2O = C_2H_5Cl + CH_3{\cdot}CO_2Et$. Methyl amyl ether, under similar conditions, yields methyl chloride and amyl acetate, together with amyl chloride and methyl acetate. C. H. B.

Psylla Wax, Psyllostearyl Alcohol, and Psyllostearic Acid (Psylla Alcohol and Psyllic Acid). III. By Ernst Edw. Sundwick (*Zeit. physiol. Chem.*, 1901, 32, 355—360. Compare Abstr., 1893, i, 125; 1898, i, 617).—Psylla wax is an ester of the composition $C_{33}H_{67}{\cdot}O{\cdot}C_{33}H_{65}O$. It is hydrolysed by hydrobromic acid, and the products are best separated, first, by solution in chloroform, and then by addition of strong sodium hydroxide to the alcoholic solution, both alcohol and acid are deposited, the latter in the form of its sodium salt, and may then be obtained by the aid of chloroform, ether, or benzene.

Psyllostearic acid, $C_{33}H_{66}O_2$, crystallises in glistening plates, melts at 94—95°, and is sparingly soluble in ether or light petroleum. Psyllostearyl alcohol, $C_{33}H_{67}{\cdot}OH$, melts at 68—70°, is soluble in light petroleum, and readily absorbs water. Its *benzoate* melts at 68—69°. J. J. S.

Study of the Perkin Reaction. By Arthur Michael [with Robert N. Hartman] (*Ber.*, 1901, 34, 918—930).—When acetic anhydride is heated for half an hour on the water-bath with dried sodium butyrate, *iso*hexoate, or *n*-hexoate, the higher anhydride is produced in almost theoretical yield; there seems to be no tendency to form the mixed anhydride, and the process furnishes a ready means of preparing the anhydrides of the acids of the acetic series. A similar reaction takes place with sodium propionate, but the yield of pure propionic anhydride is smaller, owing to the fact that its boiling point is very close to that of its lower homologue. The reverse action occurs when sodium acetate is heated with propionic anhydride at 130°, the product consisting of a mixture of acetic and propionic anhydrides. With sodium acetate and butyric anhydride, there is no interaction at 150°; at 180°, however, an almost complete double decomposition takes place, and the volatile product consists practically of acetic anhydride.

When mol. proportions of benzaldehyde, butyric anhydride, and sodium acetate are heated for 225 hours at 100°, a mixture of cinnamic and phenylangelic acids is produced, containing 1 part of the former to 14 of the latter, 1 part of cinnamic acid and 2 parts of its homologue being obtained when acetic anhydride and sodium butyrate are employed.

Benzaldehyde, when condensed with sodium acetate and *n*-hexoic anhydride, yields 1 part of cinnamic acid and 5 parts of α-butylcinnamic acid; these acids are formed in the ratio 5 : 9 when sodium hexoate and acetic anhydride are employed. *α-Butylcinnamic acid* crystallises from dilute alcohol in lustrous leaflets and melts at 83—84°. Benzaldehyde, acetic anhydride, and sodium *iso*hexoate, when heated together for 100 hours at 100° and 130 at 108°, yield a mixture of cinnamic acid (2 parts) and iso*butylcinnamic acid* (3 parts); the latter compound forms lustrous, flattened needles melting at 73°; it is readily soluble in hot water and the ordinary organic solvents. G. T. M.

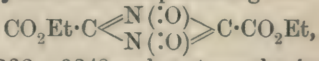
Condensation Products of Aliphatic Nitro-compounds. By ROLAND SCHOLL (*Ber.*, 1901, **34**, 862—869. Compare Dunstan and Goulding, Trans., 1900, **77**, 1262).—It is suggested that in the formation of anhydro-compounds and condensation products from aliphatic nitro-compounds, the first stage consists in the formation of an *iso*nitroso-compound, $>CH\cdot NO_2 \rightarrow >C\colon NO\cdot OH$, and that this is followed by the elimination of water, either from one mol. of the substance to form an *oxynitrile*, $R\cdot CH\colon NO\cdot OH \rightarrow R\cdot C\vdots N\colon O$, or from two mols. $2R\cdot CH\colon NO\cdot OH \rightarrow R\cdot CH\colon NO\cdot CR\cdot NO\cdot OH$, to form a condensation product. In accordance with these views, methazonic acid is regarded as a nitrogen analogue of acetoacetic acid, $CH_2\colon NO\cdot CH\colon NO\cdot OH$, and cyanomethazonic acid as $CN\cdot CH\colon NO\cdot C(CN)\colon NO\cdot OH$ or

$$CN\cdot CH\colon NO\cdot CH(CN)\cdot NO_2.$$

The compounds described in the following abstract are also regarded as products of this type of change. T. M. L.

Action of Ethyl Bromoacetate on Silver Nitrite. By ROLAND SCHOLL and ALWIN SCHÖFER (*Ber.*, 1901, **34**, 870—881).—From the interaction of ethyl bromoacetate and silver nitrite, ethyl glycollate, ethyl ethoxyacetate, ethyl glycollate nitrite and nitrate, $CO_2Et\cdot CH_2\cdot O\cdot NO$ and $CO_2Et\cdot CH_2\cdot O\cdot NO_2$, diethyl oxalate, ethyl oxynitriloformate, ethyl dioxydicyanogendicarboxylate, and a compound $C_{12}H_{15}O_8N$, are obtained.

Ethyl oxynitriloformate, $CO_2Et\cdot C\vdots N\colon O$, crystallises from hot benzene in colourless needles, melts at 111—111·5°, has a normal molecular weight as determined from the freezing point of a solution in acetic acid, and is probably formed by the loss of 1 mol. of water from ethyl dioxynitroacetate.

Ethyl dioxydicyanogendicarboxylate, a polymeride of the preceding compound, regarded as having the constitution  $CO_2Et\cdot C{<}\begin{matrix}N(\colon O)\\N(\colon O)\end{matrix}{>}C\cdot CO_2Et$, boils at 158° (corr.) under 11 mm., and at 233—234° under atmospheric pressure, and is reduced by tin and hydrochloric acid to aminoacetic acid. The *potassium* salt, $C_2N_2O_2(CO_2K)_2,3H_2O$, prepared by hydrolysis of the ester with ice-cold potassium hydroxide, is readily converted into potassium oxalate by the further action of potassium hydroxide, and explodes at 92°. The *acid*, $C_4H_2O_6N_2$, crystallises in needles and explodes at 70° or when rubbed on a rough surface. The *amide*, $C_2N_2O_2(CO\cdot NH_2)_2$, is only slightly soluble in most solvents, but crystallises from a large bulk of hot water in a snow-like form, and decomposes at 120—121°, with evolution of gas, to a liquid which solidifies on cooling (? oxamide). The *methylamide* crystallises from alcohol in needles and melts at 162°. The *benzylamide* crystallises from alcohol and melts at 174—175°. The *allylamide* is a crystalline powder melting at 95—97°. The *diethylamide* crystallises from hot alcohol in small needles and decomposes at 167°, with evolution of gas.

The *compound*, $C_{12}H_{15}O_8N$, is an oil boiling at 188—189° under 11 mm. pressure; it gives an amide by the action of strong ammonia, and is regarded as having the constitution $C_3O_2N(CO_2Et)_3$. T. M. L.

Two New Acids of the Acetylene Series. Synthesis of Octoic and Pelargonic Acid. By CHARLES MOUREU and RAYMOND DELANGE (*Compt. rend.*, 1901, **132**, 988—990).—*Amylpropiolic* [*a-octinoic*] *acid,*

$C_5H_{11}\cdot C\vdots C\cdot CO_2H$, prepared by treating sodium heptinene with carbon dioxide, is a colourless, viscid liquid, boiling at 149—149·5° under 20 mm. pressure, and having a sp. gr. 0·9677 at 18°; it solidifies in ice and then melts at 5°. When heated at 180—220°, the acid decomposes into carbon dioxide and heptinene. *Amylpropiolic chloride*, obtained by treating the preceding compound with phosphorus pentachloride, boils at 88—89° under 17 mm. pressure, and has a sp. gr. 1·0202 at 0°. The o-*toluidide* of amylpropiolic acid, produced by mixing the chloride with *o*-toluidine, melts at 59·5—60·5°; the p-*toluidide*, p-*anisidide*, and *a-naphthylamide*, melt respectively at 68°, 44°, and 113—114°.

The esters of amylpropiolic acid are prepared either by treating sodium heptinene with the alkyl chlorocarbonates, or by the interaction of amylpropiolic chloride and the corresponding alcohol. When a mixture of amylpropiolic acid and an alcohol is saturated with hydrogen chloride, the main product of reaction is the corresponding ester of the acid, $C_5H_{11}\cdot CCl{:}CH\cdot CO_2H$.

Amylpropiolic acid takes up four atoms of bromine, but the addition of the last two is a matter of some difficulty, and the reaction is always attended by an evolution of hydrogen bromide; on the other hand, the acid is readily reduced to a fully saturated acid, identical in its properties with octoic acid.

Hexylpropiolic [*noninoic*] *acid*, $C_6H_{13}\cdot C\vdots C\cdot CO_2H$, is a colourless, viscid liquid having a sp. gr. 0·9644 at 0°; it solidifies in liquid methyl chloride and melts at − 10°. When treated with sodium and boiling absolute alcohol, the compound is completely reduced, yielding pelargonic acid.

The following ethereal salts of these unsaturated acids are described in the paper:

Ester.	B. p.		Sp. gr. at 0°.
Methyl amylpropiolate ...	107°	under 20 mm.	0·9524
Ethyl ,, ...	115—116·5°	,, 17 ,,	0·9395
*iso*Propyl ,, ...	126—127°	,, 22 ,,	0·9183
*iso*Butyl ,, ...	138—139°	,, 23 ,,	0·916
*iso*Amyl ,, ...	148—149°	,, 20 ,,	0·9114
Allyl ,, ...	124—128°	,, 18 ,,	0·9465
Methyl hexylpropiolate ...	122°	,, 19 ,,	0·9338
Ethyl ,, ...	126—128°	,, 16 ,,	0·9223

G. T. M.

Hydrogenation of Amylpropiolic Acid; Hexoylacetic Acid.

By Charles Moureu and Raymond Delange (*Compt. rend.*, 1901, 132, 1121—1124).—Amylpropiolic acid (preceding abstract) is but slightly attacked by concentrated sulphuric acid, but if about 3 per cent. of sulphur trioxide is added there is an energetic reaction with formation of hexoic acid and a sulphonic acid, the barium salt of which forms slender needles slightly soluble in water.

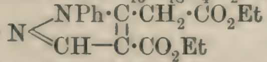
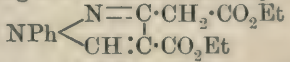
If the acid is boiled with alcoholic potash, it yields *hexoylacetic acid*, $CH_2Me\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO\cdot CH_2\cdot CO_2H$, which crystallises in white lamellæ and decomposes slowly at the ordinary temperature and rapidly at 60° into carbon dioxide and methyl amyl ketone. Its *methyl* and *ethyl* esters are more stable; the former boils at 115—116° under 14 mm. pressure and has a sp. gr. 0·994 at 0°, and the latter boils at 126—127° under 19 mm. pressure and has a sp. gr. 0·9721 at 0°. The sodium derivatives of the esters are white and insoluble; the copper derivatives are very soluble in chloroform and crystallise from alcohol in minute prisms, the derivative of the methyl ester melting at 113—114° and that of the ethyl ester at 107°.

When the chlorine derivatives of the esters of amylpropiolic acid are heated with alcoholic potash, they yield methyl amyl ketone amongst other products, and this establishes the constitution already attributed to this acid. C. H. B.

Formylacetic Esters. By Wilhelm Wislicenus and Willi Bindemann (*Annalen*, 1901, **316**, 18—42. Compare Abstr., 1887, 129).—The esters of formylacetic acid and their metallic derivatives have not been isolated in a pure state owing to their tendency to undergo condensation.

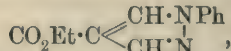
Ethyl formylglutaconate (*ethyl hydroxymethyleneglutaconate*), $OH\cdot CH{:}C(CO_2Et)\cdot CH{:}CH\cdot CO_2Et$, results from the action of dilute sulphuric acid on the sodium derivative of ethyl formylacetate dissolved in ether, and is best extracted from solution in the form of its *copper* derivative; it crystallises from ether in colourless plates and melts at 66—67°. The ester is readily soluble in the ordinary organic solvents and in sodium hydroxide solution; it cannot be distilled; its alcoholic solution develops a bluish-violet coloration with ferric chloride.

After some time, this compound changes into an oily modification, which gives a red coloration with ferric chloride. This transformation is accelerated either by the action of heat or by dissolving the substance in dilute methyl alcohol or ether; it is, however, prevented by keeping the ester in the presence of benzene. This transformation is similar to that noticed in the case of ethyl formylphenylacetate (Abstr., 1887, 129), excepting that benzene does not convert the oily form of ethyl formylglutaconate into the original solid modification. The oily form of the glutaconate slowly condenses to ethyl trimesate, this reaction being accelerated by distilling under a pressure of 1 mm. The copper derivative of ethyl formylglutaconate crystallises from benzene in moss-green leaflets and melts at 167—168°; it is far more stable on keeping than the free ester.

A *pyrazole* derivative, $C_{16}H_{18}O_4N_2$, having a constitution corresponding with either  $N{<}\begin{array}{l} NPh\cdot C\cdot CH_2\cdot CO_2Et \\ CH{-}C\cdot CO_2Et \end{array}$ or  $NPh{<}\begin{array}{l} N{=}C\cdot CH_2\cdot CO_2Et \\ CH{:}C\cdot CO_2Et \end{array}$ is obtained by the action of phenylhydrazine on ethyl formylglutaconate, the condensation being accompanied by the elimination of hydrogen and water; it separates from benzene in prismatic crystals, melts at 89—90°, and boils at 230—235° without decomposition; its solution in concentrated sulphuric acid does not develop a coloration with ferric chloride or potassium dichromate.

The crude sodium derivative of ethyl formylacetate, when boiled with excess of dilute sulphuric acid, partly condenses to trimesic acid, and partly decomposes into alcohol, acetaldehyde, and carbon dioxide.

The *phenylhydrazone* of ethyl formylacetate, $N_2HPh{:}CH\cdot CH_2\cdot CO_2Et$, obtained by the action of phenylhydrazine hydrochloride on the sodium derivative of ethyl formylacetate dissolved in water, crystallises from alcohol in yellow needles and melts at 54—57°; it changes on keeping into a dark coloured, tarry substance, and when boiled with toluene yields the compound melting at 173—174° previously described by Stolz (Abstr., 1895, i, 398).



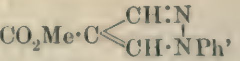
Ethyl 1-phenylpyrazole-4-carboxylate, $\mathrm{CO_2Et\cdot C}{<}\begin{matrix}\mathrm{CH\cdot NPh}\\ \mathrm{CH{:}N}\end{matrix}$, produced by distilling the preceding compound under 14 mm. pressure, crystallises from absolute alcohol in lustrous prisms and melts at 96—97°; it does not develop a coloration with ferric chloride either in alcoholic or in concentrated sulphuric acid solution. On hydrolysis with alcoholic sodium hydroxide, the ester yields the acid melting at 219—220° (compare Abstr., 1893, i, 672; 1897, i, 440).

The sodium derivative of ethyl formylacetate yields two isomeric p-*nitrobenzoates* according as to whether the reaction is carried out in ether or in water. The α-compound is formed by the action of *p*-nitrobenzoyl chloride on the sodium derivative suspended in ether; it crystallises from ether in needles melting at 87—88°; the β-isomeride is produced in aqueous solution and crystallises from ether in light red, flattened plates melting at 92—93°. Both compounds can be distilled under reduced pressure without decomposition and they give the ferric chloride reaction.

The *sodium* derivative of methyl formylacetate is obtained as a white powder by treating with sodium a mixture of methyl acetate and formate dissolved in dry ether; the free ester could not be isolated.

Methyl formylglutaconate, $\mathrm{OH\cdot CH{:}C(CO_2Me)\cdot CH{:}CH\cdot CO_2Me}$ (Abstr., 1893, i, 402) results from the action of sulphuric acid on the preceding compound; like its ethyl homologue, it slowly changes into an oily modification which develops a red coloration with ferric chloride, this transformation being accelerated by warming. This change is also accompanied by a condensation which results in the formation of methyl trimesate.

The *phenylhydrazone* of methyl formylphenylacetate, $C_{10}H_{12}O_2N_2$, separates from methyl alcohol in yellow crystals and melts at 47°, it darkens on keeping, and on boiling with toluene yields a *compound*, $C_{22}H_{20}O_4N_4$, crystallising in white leaflets from methyl alcohol and melting at 183—184°.

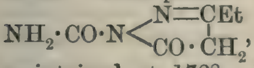


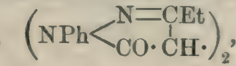
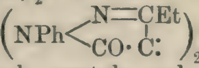
Methyl 1-phenylpyrazole 4-carboxylate, $\mathrm{CO_2Me\cdot C}{<}\begin{matrix}\mathrm{CH{:}N}\\ \mathrm{CH\cdot NPh}\end{matrix}$, obtained by distilling the preceding hydrazone under diminished pressure, crystallises from methyl alcohol in colourless needles and melts at 128—129°; it gives the pyrazoline reaction and yields the corresponding acid on hydrolysis.

The amyl esters of acetic and formic acids, when dissolved in ether, and treated with sodium, yield the *sodium* derivative of amyl formylacetate; on treatment with acid the free ester separates as an oil giving the ferric chloride reaction and yielding *amyl trimesate* on distillation under 15 mm. pressure. G. T. M.

New Reactions of Organometallic Derivatives. III. Unsubstituted β-Ketonic Esters. By EDMOND E. BLAISE (*Compt. rend.*, 1901, **132**, 978—980. Compare this vol., i, 252).—The interaction between ethyl cyanoacetate and the ether additive compounds of the magnesium alkyl iodides ($R\cdot MgI,Et_2O$), followed by the decomposition of the intermediate products by the addition of water, furnishes a general method for the preparation of the unsubstituted β-ketonic esters, $R\cdot CO\cdot CH_2\cdot CO_2Et$.

Ethyl propionylacetate and *butyrylacetate* are liquids developing red colorations with ferric chloride; sodium hydrogen sulphite combines with the former but not with the latter; the higher homologue being isolated by means of its *magnesium* derivative, a well-defined substance crystallising from methyl alcohol in needles, and melting at 156—157°. Ethyl acetoacetate, when reacting with semicarbazide, yields a semicarbazone, whereas its homologues undergo further condensation, giving rise to the amides of the corresponding pyrazolonecarboxylic acids; these compounds develop intense blue colorations with alcoholic solutions of ferric chloride. Phenylhydrazine reacts with these esters, forming pyrazolones, excess of the reagent giving rise to bispyrazolones; the latter compounds crystallise readily from a mixture of formic acid and alcohol, and are readily converted into pyrazole-blues on oxidation with potassium ferricyanide in alkaline solution.

Ethyl propionylacetate boils at 91—92° under 17 mm. and at 191° under atmospheric pressure; 3-*Ethylpyrazolone*-1-*carboxylamide*,  $NH_2\cdot CO\cdot N<\begin{matrix}N{=}CEt\\ CO\cdot\overset{|}{C}H_2\end{matrix}$, melts at 197°, but decomposes slowly when maintained at 172°. 1-*Phenyl*-3-*ethylpyrazolone* melts at 100° and develops a red coloration with alcoholic ferric chloride.

Bisphenylethylpyrazolone,  $\left(NPh<\begin{matrix}N{=}CEt\\ CO\cdot\overset{|}{C}H\cdot\end{matrix}\right)_2$, melts at 335°, and when oxidised yields the blue *compound*,  $\left(NPh<\begin{matrix}N{=}CEt\\ CO\cdot\overset{|}{C}{:}\end{matrix}\right)_2$, which separates from acetic acid in brownish-black crystals and melts at 234°.

Ethyl butyrylacetate boils at 104° under 22 mm. pressure, 3-*propylpyrazolone*-1-*carboxylamide* melts at 189°, and 1-*phenyl*-3-*propylpyrazolone* at 109—110°. The corresponding *bispyrazolone* does not melt below 335°, and its oxidation *product* crystallises from ethyl acetate in bluish-black needles and melts at 191°. G. T. M.

Action of Ethereal Alkylcyanoacetates on Diazonium Chlorides. By G. FAVREL (*Compt. rend.*, 1901, **132**, 983—985. Compare Abstr., 1900, i, 532).—The *phenylhydrazone*, $NHPh\cdot N{:}CMe\cdot CN$, of the nitrile of pyruvic acid is obtained by treating a solution of benzenediazonium chloride with methyl cyanomethylacetate and sodium hydroxide, its formation being accompanied by the elimination of methyl alcohol and carbon dioxide; it crystallises from benzene in lamellæ, and melts at 150—151°. This substance, when heated with sodium hydroxide dissolved in dilute alcohol, yields the phenylhydrazone of pyruvic acid.

The p- and o-*tolylhydrazones* produced from methyl cyanomethylacetate, and the corresponding diazonium salts, melt respectively at 166—167° and 131—132°.

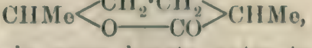
The *phenylhydrazone*, NHPh·N:CEt·CN, resulting from the interaction of ethyl cyanoethylacetate and benzenediazonium chloride, melts at 81—82°; the corresponding p- and o-*tolylhydrazones* melt at 143—144° and 114—115° respectively. G. T. M.

Dimethylpyruvic Acid. By A. Wahl (*Compt. rend.*, 1901, **132**, 1124—1126).—When dimethylpyruvic esters are treated with ammonia, the product is not dimethylpyruvamide, but a neutral crystallisable compound which melts at 198°, and can also be obtained by heating ethylaminodimethylacrylate with water in sealed tubes at 130—140°.

Attempts to decompose the acid by heating it with aniline, to convert it into *iso*butaldehyde by the action of dilute sulphuric acid, and to oxidise it by means of silver oxide gave negative results.

When treated with sodium amalgam in presence of dilute alcohol, it is converted into α-hydroxy*iso*valeric acid, and this definitely determines its constitution. C. H. B.

Methyladipic Acid from the Oxidation of Pulegone and β-Methyl*cyclo*hexanone. By Louis Bouveault and Léon Alexandre Tetry (*Bull. Soc. Chem.*, 1901, [iii], **25**, 441—444).—Contrary to the statement of Markownikoff (Abstr., 1900, i, 475), the authors find that the oxidation of β-methyl*cyclo*hexanone by nitric acid results in the formation, not of α-methyladipic acid, but of the β-acid, which was identified by means of its dianilide, melting at 198—199°. α-Methyladipic acid forms a *dianilide* crystallising in slender, white needles melting at 168°, and a *monoanilide* which forms small, white crystals melting at 122°. Adipic acid yields a *dianilide* which crystallises in small, white needles melting at 235°. These dianilides are readily prepared and purified, and are well adapted for the identification, and even the separation, of the corresponding acids. N. L.

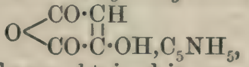
Synthesis of the αα′-Dimethyladipic Acids. By Otto Mohr (*Ber.*, 1901, **34**, 807—813).—The action of hydrogen bromide on diallyl or on methylbutallylcarbinol, $CH_2:CH\cdot CH_2\cdot CH_2\cdot CHMe\cdot OH$, yields along with the solid βζ-dibromohexane melting at 38·2° (Demjanoff, Abstr., 1891, 160) a liquid *stereoisomeride*, which boils at 94° under 13—14 mm. pressure, and does not solidify in a freezing mixture of ether and solid carbon dioxide. Both forms of βζ-dibromohexane, on converting into the corresponding nitriles by boiling for 4 hours with dilute alcoholic potassium cyanide and hydrolysing with alcoholic potassium hydroxide, yield identical products. In each case, the portion which is not volatile with steam consists of nearly equal parts of the two αα′-dimethyladipic acids, melting at 143·5° and 75—77° respectively (Zelinsky, Abstr., 1892, 430); the part volatile with steam is an acid oil which, when strongly cooled, yields crystals of *α-methyl-δ-hexolactone*,  $CHMe<\begin{matrix}CH_2\cdot CH_2\\ O\text{——}CO\end{matrix}>CHMe$, melting at 58—59°, and easily dissolving in warm baryta water to form a crystalline *barium α-methyl-δ-hydroxyhexoate.* The oil remaining after the separation of the lactone boils at 220—250°, combines additively with bromine, decolorises alkaline potassium permanganate, and is probably a mixture of *α-methyl-γδ-hexenoic acid* and *δ-ethoxy-α-methylhexoic acid*, $OEt{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe_2{\cdot}CO_2H$.

The dimethyladipic acid melting at 75—77° is largely converted into its isomeride of higher melting point when heated with water or dilute ammonia for a long period; the reverse transformation is only partially brought about by heating the form melting at 143·5° with water, either alone or with traces of ammonia, piperidine, or aniline. W. A. D.

Undecanedicarboxylic Acid and the Electrosynthesis of Decanedicarboxylic Acid. By GUSTAV KOMPPA (*Ber.*, 1901, **34**, 895—902).—Krafft and Seldis (Abstr., 1901, i, 115) did not obtain the same undecanedicarboxylic acid, when they carried out the author's synthesis of undecane-αλ-dicarboxylic acid (Abstr., 1900, i, 201). The author has repeated his experiments and obtains the same results. The melting point of the amide of undecane-αλ-dicarboxylic acid is 155—156° (not 150·5°). R. H. P.

Conversion of Tartaric Acid into Oxalacetic Acid by the Removal of Water at Low Temperatures. By ALFRED WOHL and CARL OESTERLIN (*Ber.*, 1901, **34**, 1139—1148).—*Basic pyridine diacetyltartrate*, $C_8H_{10}O_8,C_5NH_5$, obtained by the action of aqueous pyridine on diacetyltartaric anhydride, crystallises well from alcohol and melts at 121°.

When diacetyltartaric anhydride is added to anhydrous pyridine kept at −5°, the *pyridine salt* of *hydroxymaleic anhydride*,



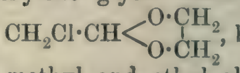
$$O\left\langle\begin{matrix}CO{\cdot}CH\\ \|\\ CO{\cdot}C{\cdot}OH,C_5NH_5,\end{matrix}\right.$$

is obtained; better yields are obtained in presence of pyridine acetate. The compound melts at 108—110°, is optically inactive, and when treated with double the theoretical quantity of 12 per cent. sulphuric acid, yields an oxalacetic acid which is identical in its properties and in those of its methyl ester with the acid obtained by Fenton and Jones (Trans., 1900, **77**, 77), except that it melts at 146°, whilst Fenton and Jones' acid has the melting point 176°. If the strength of the acid used in decomposing the pyridine salt be 30 per cent. instead of 12 per cent., an oxalacetic acid melting at 176° is obtained. This acid of higher melting point is readily transformed into that of lower by heating in aqueous solution with pyridine, acidifying with 12 per cent. sulphuric acid, extracting with ether, and crystallising.

On treating the pyridine salt of hydroxymaleic anhydride with aniline at the ordinary temperature, solution takes place with considerable heating and vigorous evolution of carbon dioxide, and on adding dilute hydrochloric acid, the anilide of pyruvic acid is obtained. When suspended in benzene and treated with acetyl chloride, the pyridine salt yields acetoxymaleic anhydride. T. H. P.

Action of Alcohols on the Acetals of Monohydric Alcohols. By MARCEL DELÉPINE (*Compt. rend.*, 1901, **132**, 968—971. Compare this vol., i, 3, 254, 314; ii, 6).—When an acetal is boiled with an alcohol in the presence of a few drops of hydrochloric acid, a double decomposition takes place, resulting in the formation of two new aldehyde ethers. The reaction is a balanced one, the product containing, in addition to the new compounds, a certain quantity of the reagents, together with the corresponding amount of the alcohol formerly combined with the original acetal. Whether methylal is heated with amyl alcohol or diamylformal with methyl alcohol, the result is the same, the product consisting of a mixture of methylal, diamylformal, methyl and amyl alcohols, and the mixed acetal, $OMe\cdot CH_2\cdot O\cdot C_5H_{11}$. Similar results are obtained with the following pairs of reagents: ethyl alcohol and diamylformal, methyl alcohol and dipropylformal, propyl alcohol and methylal. The products always contain five compounds, those of higher molecular weight predominating. When methyl or butyl alcohol reacts with diethylchloroacetal, a mixture of three chloroacetals is produced, consisting chiefly of the mixed ether; the *compound*, $CH_2Cl\cdot CH(OEt)\cdot OC_4H_9$, boils at 190—195°.

β-Naphthol reacts with the acetals, giving rise to compounds containing the aldehydic residue directly attached to the aromatic nuclei, methylal yielding 2 : 2′-dihydroxy-1 : 1′-dinaphthylmethane, whilst the anhydride of the corresponding ethane derivative, $CHMe\colon(C_{10}H_6)_2\colon O$, is obtained from acetal. Chloroacetal also gives rise to an anhydride, $CH_2Cl\cdot CH\colon(C_{10}H_6)_2\colon O$, this *compound* melting at 173—174°.

The polyhydric alcohols almost entirely displace the monohydric alcohols from their aldehyde ethers; ethylene glycol reacting on diethylchloroacetal yields the *compound*,  $CH_2Cl\cdot CH{<}\begin{matrix}O\cdot CH_2\\ |\\ O\cdot CH_2\end{matrix}$, boiling at 156—157°. Dimethylpinacone replaces methyl and ethyl alcohols in a similar manner, and in this way its *chloroacetal*, *acetal*, and *formal* ethers have been prepared; they are liquids boiling respectively at 191—192°, 134°, and 124—125°. The *chloroacetal* of glycerol boils at 235—240°. Erythritol reacting with acetal gives rise to the *diacetal* melting at 95° and the *monoacetal*, $C_4H_8O_4\cdot C_2H_4$, melting at 102°; its *dichloroacetal*, $C_4H_6O_4(C_2H_3Cl)_2$, melts at 101—103°.

The reactions between mannitol and the acetals are more complicated, and a certain amount of the alcohol changes into mannitan; nevertheless, the *triacetal*, melting at 171—173°, was isolated from the products of reaction with acetal, whilst the *dichloroacetal*, $C_6H_{10}O_6(C_2H_3Cl)_2$, melting at 135°, was obtained by the action of chloroacetal.

G. T. M.

Bromide and Iodide of Acetylchloral. By Emilio Gabutti and G. Bargellini (*Gazzetta*, 1901, 31, i, 82—85).—*Acetylchloral bromide* (*a-bromo-$\beta\beta\beta$-trichloroethyl acetate*), $CCl_3\cdot CHBr\cdot OAc$, prepared by the action of acetyl bromide on chloral, is a heavy, colourless oil with a pleasant odour resembling that of the corresponding chloride; it distils undecomposed at 106° under a pressure of 735 mm. of mercury, and is extremely soluble in alcohol, ether, or chloroform, but insoluble in water. With cold dilute alkali hydroxide solutions, it has no action, but with hot concentrated solutions it yields chloroform.

Acetylchloral iodide (*a-iodo-$\beta\beta\beta$-trichloroethyl acetate*), $CCl_3\cdot CHI\cdot OAc$, prepared from acetyl iodide and chloral, is a dense oil from which the free iodine could not be completely removed. It readily decomposes on heating, even under reduced pressure.

T. H. P.

Action of Alcohols on Chloral. By EMILIO GABUTTI (*Gazzetta*, 1901, **31**, i, 86—92).—*Chloral propylate* (*α-hydroxy-α-propoxy-βββ-trichloroethane*), $CCl_3\cdot CH(OH)\cdot OPr$, prepared by the action of propyl alcohol on chloral, is a dense, colourless liquid with an odour faintly recalling that of propyl alcohol; it boils at 120—122°, and is very soluble in alcohol or ether, but insoluble in water. The action of acetyl chloride on chloral propylate yields the following three compounds. (1) Acetylchloral chloride, (2) propyl acetate, and (3) *acetylchloral propylate* (*α-acetoxy-α-propoxy-βββ-trichloroethane*),

$$CCl_3\cdot CH(OAc)\cdot OPr,$$

which is a colourless liquid boiling at 114—116°; it does not dissolve in water, but is extremely soluble in alcohol or ether, and has a pleasant odour recalling that of acetic acid.

Chloral iso*propylate* (*α-hydroxy-α-*iso*propoxy-βββ-trichloroethane*), $CCl_3\cdot CH(OH)\cdot OPr^\beta$, obtained by the action of *iso*propyl alcohol on chloral, is a colourless liquid with an odour resembling that of *iso*propyl alcohol; it boils at 108°, and, on cooling with ice and salt, crystallises to a mass of small, white needles melting at 47°; it is extremely soluble in alcohol or ether, but insoluble in water. The only compound which could be separated from the products of the action of acetyl chloride on chloral *iso*propylate was *iso*propyl acetate.

Trimethylcarbinol could not be made to react with chloral, even when the two compounds were heated together in a sealed tube at 150—180°. This alcohol, hence, resembles the phenols in this respect.

T. H. P.

Methyl Nonyl Ketone. By HENRI CARETTE (*J. Pharm.*, 1901, [vi], **13**, 412—415).—Cinnamaldehyde condenses with methyl nonyl ketone under the action of alcoholic potash. The *product* forms white, lustrous needles melting at 87°. By changing the conditions, no other substance can be obtained. The author has shown that benzaldehyde and methyl nonyl ketone give more than one condensation product.

K. J. P. O.

Oxime of Diacetonamine. By M. KOHN (*Ber.*, 1901, **34**, 792—794).—The author has prepared diacetonaminoxime (Harries, this vol., i, 194) independently by dissolving diacetonamine oxalate in hot water, cooling, adding concentrated aqueous potassium hydroxide, and then aqueous hydroxylamine hydrochloride, both gradually and with constant shaking; the product is eventually extracted with ether and distilled under diminished pressure. When dissolved in 10 per cent. aqueous sodium hydroxide and shaken with benzoyl chloride, it readily forms a *dibenzoyl* derivative, $NHBz\cdot CMe_2\cdot CH_2\cdot CMe{:}NOBz$, which melts at 121—123°.

C. F. B.

Fermentation of Pentoses. By A. SCHÖNE and BERNHARD TOLLENS (*J. Landw.*, 1901, **49**, 29—40).—According to Scheibler, von Lippmann, Stone and Tollens, and Lindner, arabinose does not ferment with yeast. Frankland and MacGregor (Trans., 1892, **61**, 737) found that *Bacillus ethaceticus* decomposes arabinose with production of alcohol, acetic, formic, and succinic acids, carbon dioxide and hydrogen.

Cross and Bevan (*Jour. Fed. Inst. Brewing*, 1897, 3, No. 1) state that during the fermentation of worts, a portion of the pentoses or pentosans disappears, along with the maltose. Salkowski (Abstr., 1900, i, 628) found that arabinose, in presence of putrefying meat, was decomposed into alcohol, volatile acids (especially acetic acid), and non-volatile acids, including succinic acid. Xylose seemed to yield the same products.

Extracts (with boiling 3 per cent. sulphuric acid) of jute and brewers' grains, neutralised with calcium carbonate, were subjected to the action of lager beer yeast for some days at 26—27°. A considerable reduction in the amount of pentosans took place, and, coincidently, alcohol and acetic and lactic acids were formed. Similar results were obtained with pure yeast (Hansen's).

In the case of pure arabinose, pure yeast had practically no effect, but an organism from sour milk decomposed arabinose, with production of alcohol and acids. N. H. J. M.

Rhodeose, a Methylpentose from Convolvulin. By Emil Votoček (*Zeit. Zuckerind. Böhm.*, 1901, 25, 297—305. Compare Abstr., 1900, i, 332).—The following derivatives of rhodeose have been prepared. The *phenylmethylhydrazone*, $C_6H_{12}O_4{:}N_2MePh$, separates from alcohol in colourless, silky needles melting at 181—182°. The *phenylethylhydrazone* crystallises from alcohol in shining, colourless needles melting at 193°. The p-*bromophenylhydrazone* separates from dilute alcohol in yellowish crystals which have a silky lustre and melt at 184°. The *phenylbenzylhydrazone* is deposited from alcohol in nearly white crystals melting at 178—179°.

By the action of benzaldehyde on the phenylmethylhydrazone, rhodeose is obtained, and slowly crystallises in stellate aggregates of microscopic, anhydrous needles. Aqueous solutions of the sugar show mutarotation, the final value of $[\alpha]_D$ being $+75{\cdot}2°$; the lower number previously obtained (*loc. cit.*) seems to be due to the presence in crude rhodeose of another methylpentose having a lower rotation.

Various colour reactions of crystallised rhodeose are described. Rhodeose reduces Fehling's solution and ammoniacal silver solution; methylfurfuraldehyde is formed when a solution of the sugar is boiled with 12 per cent. hydrochloric acid solution. T. H. P.

Refraction of Aqueous Carbohydrate Solutions. I. Mutarotating Sugars (Hexoses). By F. Stolle (*Zeit. Ver. deut. Zuckerind.*, 1901, 335—347).—In order to obtain evidence as to the nature of the changes occurring in solutions of sugars exhibiting mutarotation, the author has determined the alteration in specific gravity, and hence in concentration and also in the refraction, of solutions of lævulose, dextrose, and galactose when kept for 24 hours. The anhydrous sugars were used and a number of solutions varying in concentration from about 1 to about 20 per cent. were examined, the temperature in all cases being 17·5°.

Seven solutions of lævulose were prepared, and the concentration (grams per 100 c.c.) at various times after making the solutions are given in the following table :

	1.	2.	3.	4.	5.	6.	7.
10 minutes........	1·0090	2·0100	4·0110	8·0073	12·0250	15·9990	25·0160
6 hours	1·0091	2·0100	4·0116	8·0074	12·0263	15·9999	25·0190
24 hours	1·0091	2·0105	4·0124	8·0091	12·0275	16·0055	25·0187

It will be seen that in each solution an increase takes place in the proportion of active substance present, and this is accompanied by a corresponding increase in the index of refraction as is shown by the following values of n_D for the various solutions:

	1.	2.	3.	4.	5.	6.	7.
10 minutes........	1·33448	1·33596	1·33872	1·34447	1·35008	1·35572	1·36825
24 hours	1·33448	1·33595	1·33882	1·34456	1·35036	1·35591	1·36844

The quotient obtained by dividing the difference between the refractive index of any solution and that of water by the concentration, has a constant value of about 0·00141 for all the solutions. The specific refraction (Lorentz and Lorenz formula) of lævulose in the solutions examined does not vary either with the concentration or with time, the value in all cases being about 0·206.

The results obtained with dextrose and galactose are strictly comparable with the above, the quotient of the increment of refractive index by concentration having about the same value, 0·00141 and the specific refraction being approximately 0·206.

These results are all in favour of the hydrate theory according to which the anhydrous sugar takes up a molecule of water to form the heptahydric alcohol, $C_6H_{14}O_7$, having a lower rotatory power than the sugar. T. H. P.

Dextrose. By Ferdinand von Arlt (*Monatsh.*, 1901, **22**, 144—150).—By the action of phosphorus pentachloride on pentacetyldextrose dissolved in dry chloroform in the presence of aluminium chloride, acetochlorohydrose is obtained. It crystallises from ether in needles melting at 72—74° and having $[\alpha]_D + 165·76°$ at 20°. On reduction with zinc dust and iron filings in acetic acid solution, a pentacetylhexose is obtained which appears to be identical with α-pentacetyldextrose described by Franchimont (Abstr., 1893, i, 246). Hydrolysis with sulphuric acid converts it into a sugar, which yields phenylglucosazone with phenylhydrazine. K. J. P. O.

Derivatives of Dextrose and of Galactose. By Wilhelm Koenigs and Eduard Knorr (*Ber.*, 1901, **34**, 957—981. Compare Ryan, Trans., 1899, **75**, 1054).—*Tetracetylbromodextrose*, $C_6H_7OBr(OAc)_4$, obtained when dextrose (1 mol.) is treated with acetyl bromide (5 mols.), crystallises from dry ether in glistening, white needles melting at 88—89°, is readily soluble in most organic solvents, and has $[\alpha]_D + 198°10'$ at 19°. It is slowly hydrolysed by water, reduces boiling

Fehling's solution, and the bromine is as readily replaceable as the chlorine in tetracetylchlorodextrose. When its solution in glacial acetic acid is shaken with silver acetate, pentacetyldextrose is formed. With methyl alcoholic solutions of potassium phenoxide and β-naphthoxide, it yields phenylglucoside (compare Michael, Abstr., 1885, 521) and β-naphthylglucoside (Ryan). When left in contact with absolute methyl alcohol for several days, it yields β-methylglucoside melting at 108—110° (Abstr., 1895, i, 5). When shaken with absolute methyl alcohol and dry silver carbonate, it yields *tetracetyl-β-methylglucoside*, $OMe{\cdot}C_6H_7O(OAc)_4$. This crystallises from methyl alcohol in large, glistening, rhombic crystals $[a : b : c = 0{\cdot}7634 : 1 : 0{\cdot}4638]$, dissolves readily in most solvents; it sinters at 102°, melts at 104—105°, has $[\alpha]_D$ $-23°6'$ at 15°, has no reducing action on boiling Fehling's solution, and is readily hydrolysed by alkali to β-methylglucoside. The same compound is formed when a concentrated aqueous solution of silver nitrate acts on a methyl alcoholic solution of tetracetylbromodextrose, and also when the bromo-compound is treated with a methyl alcoholic solution of pyridine. *Tetracetyl-α-methylglucoside*, obtained by the acetylation of E. Fischer's α-methylglucoside (Abstr., 1895, i, 438), melts at 101°, and has $[\alpha]_D$ $+175°35'$ at 20°. *Tetracetyl-β-ethylglucoside* crystallises from alcohol in colourless prisms, melts at 106—107°, has $[\alpha]_D$ $-27°4'$ at 16·5°, and when hydrolysed with alkali yields β-ethylglucoside in the form of a syrup having $[\alpha]_D$ $-30°7'$ at 20°, which is readily decomposed by emulsin, but not by yeast enzymes.

Acetonitroglucose (tetracetyldextrose nitrate), melting at 150—151° (Colley 145°), may be obtained by the action of a solution of fuming nitric acid in chloroform on the bromo-compound or on the pentacetyldextrose melting at 130—131°, but not on the pentacetyl compound melting at 112° (Erwig and Koenigs, Abstr., 1889, 952). The nitro-compound is readily soluble in most organic solvents, with the exception of light petroleum, and has $[\alpha]_D$ $+149°19'$ at 18°; it reduces boiling Fehling's solution, and when dissolved in glacial acetic acid gives a red coloration with brucine. When heated with dry sodium acetate and acetic anhydride, it is reconverted into the pentacetyldextrose. When warmed with methyl alcohol and either pyridine or barium carbonate, it yields tetracetyl-β-methylglucoside.

Acetonitrogalactose (*tetracetylgalactose nitrate*), $NO_2{\cdot}O{\cdot}C_6H_7O(OAc)_4$, obtained from Erwig and Koenig's pentacetylgalactose, melts at 93—94°, and has $[\alpha]_D$ $+153°13'$ at 20°. When warmed with methyl alcohol and barium carbonate, it yields *tetracetyl-β-methylgalactoside*, which melts at 93—94°, and has $[\alpha]_D$ $-25°28'$ at 17°; this does not reduce Fehling's solution, and does not give the brucine test.

J. J. S.

Cellose, a Biose from Cellulose. By ZDENKO H. SKRAUP and J. KÖNIG (*Ber.*, 1901, 34, 1115—1118).—The acetyl derivative obtained by the action of acetic anhydride and concentrated sulphuric acid, and regarded as a monose derivative owing to the results of molecular weight determinations being in correspondence with a pentacetylhexose (See Skraup, Abstr., 1899, i, 852), is now shown to be a biose, and the name *cellose* is given to it. In freezing phenol, the acetyl compound has the mean molecular weight 546, in freezing acetic acid 572, whilst boiling point measurements give the numbers 663, 640 and 666 for the solvents benzene, chloroform, and ethyl acetate respectively; the value for an octacetylbiose is 678. On treating the acetate with concentrated alcoholic alkali hydroxide, the cellose is obtained, and after repeated crystallisation from dilute alcohol, it forms a fine, snow-white powder consisting of microscopic, irregular prisms or plates, which retain $\frac{1}{4}H_2O$ when dried in a vacuum, but become anhydrous and faintly yellow on heating at 100°. The new sugar has not a characteristic taste, the after taste being faintly sweet. Its aqueous solution rapidly reduces Fehling's solution, but is only slightly, if at all, fermented by yeast. It shows distinct birotation and has $[\alpha]_D$ +33·7° in a 9·4766 per cent. solution at 20°. When hydrolysed, cellose yields dextrose and possibly another sugar.

Just in the same way as maltose is the simplest polysaccharide obtained from starch, so is cellose the simplest from cellulose. Cellulose and starch are hence fundamentally different substances, and the former cannot be regarded as a highly polymerised form of the latter. That it is improbable that any intramolecular rearrangement occurs when octacetylcellose is hydrolysed with alcoholic alkali hydroxide is shown by submitting the α- and β-acetyl compounds of dextrose to the same treatment, the product in each case consisting almost entirely of dextrose. T. H. P.

Molecular Weight of Glycogen. By HENRY JACKSON (*Proc. Camb. Phil. Soc.*, 1901, **11**, 115—116).—A sample of glycogen was very carefully purified, in particular from inorganic salts, and was then found to lower the freezing point of water by an amount corresponding with a molecular weight of 9500—10000. C. F. B.

Estimation of Pentosans by the Hydrochloric Acid Phloroglucinol Method. By E. KRÖBER (*J. Landw.*, 1901, **49**, 7—20. Compare this vol., ii, 288).—The dry matter of different woods was found to contain the following amounts of pentosans: fir, 11·62; beech, 25·91 (=23·58 per cent. of xylan); and guaiac 18·16 per cent. (compare Councler, *Chem. Zeit.*, 1894, 966, and *Mündener Forstl. Hefte.*, **11**, 21, and **12**, 79; Flint, *Inaug. Diss. Göttingen*, 1892.

Dry wood gum, free from ash, from beech wood and wheat straw yielded 82·3 to 88·1 per cent. of xylan (compare Rimbach, *Diss. Göttingen*, 1898).

Determinations of pentosans were made in "crude fibre" prepared by Henneberg's method, by König's method (boiling with glycerol-sulphuric acid, *Zeit. Unters. Nahr.-und Genussmittel*, 1898, 3), and by Lebbin's hydrogen peroxide method (*Arch. Hyg.*, **28**, 212). The "crude fibre" from meadow hay and from wheat meal prepared by Henneberg's method yielded 3·97—4·29 and 0·24—0·25 per cent. of pentosans. Lower results were obtained with "crude fibre" prepared by König's method (from rye straw, wheat bran, wheat meal, hay, and cotton seed meal), the percentages of pentosans being 0·25 to 0·80). Lebbin's process yielded "crude fibre" from rye straw containing 26·98—27·00 per cent. of pentosans.

Cotton-wool yielded 0·61 per cent. of furfuraldehyde; oxycellulose prepared from the same cotton-wool yielded 1·86, 0·69, and 1·42 per cent.; whilst a calcium salt from oxycellulose yielded 3·24 per cent. of furfuraldehyde (compare Gans, *Diss. Göttingen*; Rimbach, *loc. cit.*; Sestini, *L'Orosi*, 1898; and Suringar, *Diss. Göttingen*, 1896).

Determinations of water, ash, and pentosans were made in papers employed for newspapers in Germany, Holland, and Canada. From the results obtained, estimations are made of the probable percentages of wood and of sulphite-cellulose in the paper. A number of samples of writing and other papers were also examined. All the papers contained more than 5 per cent. of pentosans (in dry substance free from ash) and most contained more than 10 per cent.; in one case, as much as 12·9 per cent. was found. N. H. J. M.

Behaviour of Aqueous Formaldehyde towards Gun-cotton. By Ludwig Vanino (*Ber.*, 1901, **34**, 1128).—When gun-cotton is moistened with a 20 per cent. aqueous solution of formaldehyde and then allowed to dry, either at the ordinary temperature or on the water-bath, it loses its capacity of exploding by percussion, without apparently being decomposed. If the paraformaldehyde is removed from the gun-cotton either by boiling with water or by heating the cotton, it is found that the original explosibility is regained.

T. H. P.

New Base Derived from Glucose. By Léon Maquenne and E. Roux (*Compt. rend.*, 1901, **132**, 980—983. Compare Fischer, Abstr., 1887, 567).—*Glucamine*, $OH\cdot CH_2\cdot[CH\cdot OH]_4\cdot CH_2\cdot NH_2$, is produced by reducing dextroseoxime in a cold 10 per cent. aqueous solution with 3 per cent. sodium amalgam, sulphuric acid being slowly added during the reaction in order to neutralise the sodium hydroxide produced. It is isolated by means of its *neutral oxalate*, $2C_6H_{15}NO_5,H_2C_2O_4$, a substance crystallising from dilute alcohol in glistening, hexagonal plates. The base itself, obtained as a mass of ill-defined crystals by treating the oxalate with an equivalent amount of calcium hydroxide, melts at 127—128°, is soluble in water and alcohol, but not in ether. In a 10 per cent. aqueous solution it has $[\alpha]_D$ $-8°$ and does not exhibit mutarotation.

The base has a sweet and caustic taste, it absorbs carbon dioxide and yields salts which are all soluble in water but not in alcohol, the latter solvent precipitating them from their aqueous solutions in a syrupy condition. The yellow picrate is amorphous and the platinichloride crystallises with difficulty.

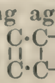
An *oxamide* having the composition $C_{14}H_{28}O_{12}N_2$, and $[\alpha]_D$ $-15·3°$ is obtained by heating the oxalate at 180°.

Glucamine does not reduce Fehling's solution, and behaves like ammonia in precipitating the hydroxides from solutions of the metallic salts; ferric hydroxide, however, redissolves, yielding a brown solution; with copper sulphate, it yields a blue solution which deposits small, blue crystals; mercuric chloride and silver nitrate give white precipitates, that derived from the latter reagent giving rise to a mirror on warming. Glucamine gives the iodoform reaction on boiling with iodine solution; it is only slowly attacked by nitrous acid in the cold, at higher temperatures, however, the reaction is more rapid, and a mixture of lævorotatory reducing sugars is produced which yields glucosazone on treatment with phenylhydrazine acetate. Towards ethyl oxalate, benzaldehyde, acetylacetone, and potassium cyanate, glucamine behaves as a primary base and yields crystallisable products with these reagents. The absence of mutarotation shows that the geometrical configuration of the base is stable in aqueous solution; in this respect the compound resembles the hexatomic polyhydric alcohols and differs from chitosamine which contains a carbonyl group. G. T. M.

Action of Reducing Gases on Thiocyanates. By JAMES T. CONROY, OLIVER HESLOP, and J. B. SHORES (*J. Soc. Chem. Ind.*, 1901, **20**, 320—322).—On passing dry hydrogen through molten potassium thiocyanate previously dried at 100° and heated at 600°, decomposition is complete after 2½ hours. Calculated in terms of the percentage of thiocyanate decomposed, the product contains potassium cyanide 71, hydrogen sulphide 71, hydrogen cyanide 18, potassium sulphide 24, and ammonia 6·5, showing that decomposition occurs principally according to the equation $KCNS + H_2 = H_2S + KCN$, and partially thus, $2KCN + H_2S = K_2S + 2HCN$ (compare Sestini and Funaro, Abstr., 1882, 1180, and Playfair, *J. Soc. Chem. Ind.*, 1892, **11**, 14). Ninety-six per cent. of the total nitrogen is thus accounted for, and 95 per cent. of the total sulphur; the origin of the ammonia is uncertain, but is probably due to water being present. Conversely, when dry hydrogen sulphide is passed into fused potassium cyanide at a dull red heat, hydrogen cyanide is evolved, but two-thirds of the cyanide is converted into thiocyanate, owing probably to the hydrogen sulphide initially dissociating into hydrogen and sulphur.

With sodium thiocyanate, hydrogen yields much less metallic cyanide and hydrogen sulphide than with the potassium salt, more ammonia and more of the metallic sulphide being formed. Calcium thiocyanate yields only traces of hydrogen cyanide and sulphide, white fumes being evolved which are not soluble in dilute acid or alkali. The product remaining consists entirely of calcium sulphide. With barium and copper thiocyanates, the metallic sulphides only are formed, hydrogen cyanide and hydrogen sulphide being evolved along with other volatile products. W. A. D.

The Benzene Problem from the Stereochemical Standpoint. By EMIL ERLENMEYER, jun. (*Annalen*, 1901, **316**, 57—71).—A discussion of the molecular configuration of benzene, illustrated by diagrams of space formulæ not suitable for abstraction. G. T. M.

The Closer Coalescence of the Multivalent Atoms of Molecular Systems containing Neighbouring Double-linkings. By EMIL ERLENMEYER, jun. (*Annalen*, 1901, **316**, 71—74).—The formation of ringed systems of the benzene type illustrates the tendency which the carbon atoms of unsaturated compounds possess of becoming interlinked to the maximum extent. Assuming that this tendency is general, a ready explanation is furnished of the behaviour of compounds containing the residue $-C{:}C\cdot C{:}C-$ towards reducing agents; this configuration changes to that of the closed chain system,  $\begin{matrix}C\cdot C- \\ | \quad | \\ C\cdot C-\end{matrix}$, and the hydrogen atoms become attached to the carbon atoms which were originally at the end of the open chain. This assumption renders the hypothesis of partial valency superfluous (compare Thiele, Abstr., 1899, i, 554, and Knoevenagel, Abstr., 1900, ii, 534) and readily explains the reduction of benzil and the formation of *d*- and *l*-*iso*hydrobenzoin and hydrobenzoin from benzaldehyde. G. T. M.

4-Hydroxyhydrindene. New Derivatives of Xylene and Ethylbenzene. By J. Moschner (*Ber.*, 1901, 34, 1257—1262. Compare Abstr., 1900, i, 344).—Hydrindene-4-sulphonic acid was found in the liquors obtained on sulphonating ψ-cumene, and its constitution determined by oxidation to a sulphophthalic acid which gave 3-hydroxyphthalic acid when fused with potassium hydroxide.

4-*Hydroxyhydrindene*, prepared by fusing the sulphonic acid with potassium or sodium hydroxide, is an oil which boils at 244—246°, does not solidify on cooling, and has an odour resembling that of phenol. 4-*Methoxyhydrindene* is an aromatic oil boiling at 225—227°.

1 : 3-*Xylene*-5-*sulphinic acid*, prepared by Gattermann's method from *s*-*m*-xylidine, melts at 75—76°, or 2° lower than the 1 : 3 : 4-acid (Gattermann, Abstr., 1899, i, 517).

1 : 3-*Xylene*-5-*sulphonic chloride* crystallises from ether and melts at 89—90°. The *sulphonamide* crystallises from hot water in needles and melts at 135°.

1 : 2-*Xylene*-3-*sulphinic acid* melts at 105°, and on oxidation forms the 1 : 2 : 3-sulphonic acid.

The melting points of the sulphonamides of this series are 60—63° higher than those of the sulphinic acids in each of the five cases where data are available.

Ethyl-4-*anisole* is an aromatic liquid which boils at 199—200°, and when oxidised yields *p*-methoxybenzoic acid. Ethyl-4-phenetole boils at 211° and not at 200° (Errera, Abstr., 1885, 775).

T. M. L.

Action of Ethylidene Chloride and Methylene Chloride on Naphthalene in Presence of Aluminium Chloride. By F. Bodroux (*Bull. Soc. Chim.*, 1901, [iii], 25, 491—497).—The action of ethylidene chloride on naphthalene in the presence of aluminium chloride results in the production of β-methylnaphthalene together with small quantities of α-methylnaphthalene, α- and β-ethylnaphthalenes, dimethylnaphthalenes, and ββ-dinaphthyl; a large quantity of methane is also evolved. The principal products of the action of methylene chloride on naphthalene are β-methylnaphthalene and ββ-dinaphthyl. Full details of the separation and identification of these products are given in the paper. N. L.

Triphenylchloromethane. By Moses Gomberg (*J. Amer. Chem. Soc.*, 1901, 23, 109—110).—A polemical reply to Norris and Sanders (Abstr., 1901, i, 198). E. G.

Tritolylchloromethane. By Moses Gomberg and O. W. Voedisch (*J. Amer. Chem. Soc.*, 1901, 23, 177—178).—*Tritolylchloromethane* may be obtained by the action of aluminium chloride on a mixture of carbon tetrachloride and toluene, the method employed being that previously described for the preparation of the corresponding triphenyl-compound (Gomberg, Abstr., 1901, i, 77). When boiled with alcohol, it yields the *ethoxy*-derivative melting at 105°, and if boiled with water, the *carbinol* is produced. E. G.

Oxidation of Aniline. By Ernst Börnstein (*Ber.*, 1901, **34**, 1268—1274).—When dioxide of lead or manganese is added gradually to a neutral aqueous solution of aniline hydrochloride or sulphate, azophenine melting at 246° and aminoquinonediphenylimide are produced together with some azobenzene.

Aminoquinonediphenylimide, $NH_2\cdot C_6H_3(NPh)_2$, crystallises in stellate groups of dull red prisms with a faintly bluish tint, melts at 167°, and is readily soluble in most organic solvents but only sparingly in methyl or ethyl alcohol. It dissolves in concentrated sulphuric acid to form a red solution which becomes blue when heated, and on dilution yields a blue solution with a red fluorescence. It is decomposed by dilute mineral acids and also by acetic acid. When reduced with alcoholic ammonium sulphide and the product distilled under reduced pressure in an atmosphere of coal gas, a residue is obtained which yields a *substance*, $NH_2\cdot C_6H_3(NHPh)_2$, crystallising in aggregates of lustrous needles and melting at 83°; its *acetyl* derivative, $NHAc\cdot C_6H_3(NHPh)_2$, crystallises in colourless, six-sided plates, melts at 170—171°, and dissolves readily in alcohol, ethyl acetate, benzene, acetone, or chloroform.

When aminoquinonediphenylimide is heated with aniline in presence of aniline hydrochloride or zinc chloride, it is converted into azophenine. E. G.

Aniline and Quinoline Derivatives of Metallic Trichlorides. By Hugo Schiff (*Ber.*, 1901, **34**, 804—805).—Some of the compounds described by Vanino and Hauser (Abstr., 1900, i, 641; this vol., i, 289) were prepared long ago by the author. The chloride and the base were made to unite in benzene solution by the aid of heat; from dilute hydrochloric acid they sometimes crystallised with HCl (and H_2O). The compounds cited are $BiCl_3,3(NH_2Ph,HCl),3H_2O$; $BiCl_3,3(NH_2Ph,HCl)$; $BiCl_3,3(C_9H_7N,HCl)$; $SbCl_3,3NH_2Ph$, melting at 80°; $SbCl_3,3(NH_2Ph,HCl),3H_2O$; $SbI_3,3(NH_2Ph)$. C. F. B.

Oxidation of *p*-Toluidine. By Ernst Börnstein (*Ber.*, 1901, **34**, 1274—1284).—By the action of potassium dichromate on *p*-toluidine sulphate, Perkin (Trans., 1880, **37**, 546) obtained two compounds which he regarded as tri-*p*-tolylenetriamine and tolyltri-*p*-tolylenetriamine; the former substance, which had been previously obtained by Barsilowski (Abstr., 1873, 273) was shown by Green (Trans., 1893, **63**, 1395) to be amino-*p*-toluoquinoneditolylimide. The same two compounds have been obtained by the author by the action of lead dioxide on a neutral solution of *p*-toluidine hydrochloride or sulphate, *p*-ditolylamine and small quantities of *p*-azotoluene being simultaneously produced, whilst the employment of manganese dioxide under certain conditions resulted in the formation of aminotoluoquinoneditolylimide and azotoluene.

Amino-*p*-toluoquinoneditolylimide melts at 235°. When heated with a mixture of *p*-toluidine, *p*-toluidine hydrochloride, and alcohol, it yields the *hydrochloride* of a base, crystallising in yellow plates and melting at 282°; the *base* itself, $NH_2\cdot C_7H_3(N\cdot C_7H_7)_2(NH\cdot C_7H_7)_2$, crystallises from alcohol in orange-red leaflets and melts at 250—251°. The formation of the hydrochloride is accompanied by that of another *substance* which forms yellowish-red crystals and melts at 321—322°.

p-Toluidino-*p*-toluoquinoneditolylimide, $C_7H_7\cdot NH\cdot C_7H_5(N\cdot C_7H_7)_2$, identical with the second substance described by Perkin (*loc. cit.*), melts at 183°; if it is dissolved in alcoholic sulphuric acid (5 per cent.), left for 24 hours, and then saturated with ammonia, on dilution with water a precipitate is produced of a *base*,

$$C_7H_7\cdot NH\cdot C_7H_5O(N\cdot C_7H_7),$$

which crystallises from hot alcohol in lustrous, dark reddish-brown needles, melts at 181°, and dissolves readily in benzene, toluene, chloroform, acetone, or ether; small quantities of another *compound* are simultaneously formed, which is obtained in tabular, red crystals with a bluish tint. The former substance yields a well-crystallised *hydrochloride*, *sulphate*, and *platinichloride*; if it is dissolved in concentrated sulphuric acid, a green solution is obtained, which on dilution with water forms an orange-yellow solution containing the sulphate of a new, yellow, crystalline *base*. E. G.

[Action of Cyanogen Bromide on Dimethylaniline]. By Roland Scholl and Wilhelm Nörr (*Ber.*, 1901, 34, 1345).—Methylcyanoaniline (phenylmethylcyanamide), described by the authors as a new substance (Abstr., 1900, i, 435), has previously been prepared by Wallach (Abstr., 1899, i, 659) and by Stieglitz and MacKee (Abstr., 1900, i, 340). K. J. P. O.

Substituted Ammonium Compounds of the Type $NR'R''R'''_2X$. By Humphry O. Jones (*Proc. Camb. Phil. Soc.*, 1901, 11, 111—114).—*Phenylbenzyldimethylammonium iodide* is formed from dimethylaniline and benzyl iodide, or, better, from benzylmethylaniline and methyl iodide; the same product is obtained in both cases, even at 0°. It melts at 163—164°; the corresponding d-*camphorsulphonate* obtained from it by treatment with silver camphorsulphonate and moist ethyl acetate, melts and decomposes at 189°.

Phenyldibenzylmethylammonium iodide is formed from benzylmethylaniline and benzyl iodide, and melts at 134—135°; the *chloride*, obtained from it by double decomposition with silver chloride, melts at 160—161°; the d-*camphorsulphonate* melts at 135—138° and crystallises with $1CHCl_3$; the d-*bromocamphorsulphonate* was not obtained crystalline. The chloride cannot be obtained from benzylmethylaniline and benzyl chloride, either at the ordinary temperature or at 100°, and the iodide cannot be prepared from dibenzylaniline and methyl iodide; at 100°, phenyltrimethylammonium iodide is obtained instead. C. F. B.

Study of Aldehydes: Compounds of Schiff's Bases with Sulphurous Acid and the Alkali Hydrogen Sulphites. By Alexander Eibner (*Annalen*, 1901, 316, 89—143).—*Ethylideneaniline hydrogen sulphite*, $NPh\colon CHMe,H_2SO_3$, prepared either by adding acetaldehyde to a solution of aniline in excess of sulphurous acid or by shaking ethylideneaniline with a solution of this acid, crystallises in colourless, prismatic needles melting at 94°; it can be crystallised from alcohol without alteration, but decomposes in contact with water or aqueous solutions of ammonia and sodium hydroxide, regenerating the ethylidene base. *Ethylideneaniline sodium sulphite*, formed either by treating the preceding compound with sodium carbonate solution or by adding aniline to the sodium hydrogen sulphite compound of acetaldehyde dissolved in water, crystallises in snow-white, lustrous leaflets; it readily dissolves in water, yielding a neutral solution from which the hydrogen sulphite compound is precipitated by the cautious addition of dilute hydrochloric acid. These reactions indicate that these compounds are constituted on the type of sulphonates having respectively constitutions represented by the following formulæ, $SO_2{<}\begin{matrix}CHMe\\O\end{matrix}{>}NH_2Ph$ and $ONa\cdot SO_2\cdot CHMe\cdot NHPh$.

Neutral anhydroformaldehyde aniline hydrogen sulphite,

$$(CH_2{:}NPh)_2H_2SO_3,$$

obtained by adding formaldehyde solution to an aqueous sulphurous acid solution of aniline containing excess of the base, crystallises in snow-white leaflets and decomposes at 129—130°; it gradually changes into a yellow, amorphous, insoluble substance which does not regenerate the aldehyde on heating with dilute sulphuric acid; the original compound is regarded as having the constitution

$$CH_2{:}NHPh\cdot SO_2\cdot O\cdot NHPh{:}CH_2,$$

whilst the product of transformation is in all probability a derivative of diphenylmethane.

Anhydroformaldehydeaniline sodium hydrogen sulphite,

$$CH_2{:}NPh,HNaSO_3,$$

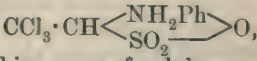
obtained by Hofer from anhydroformaldehydeaniline, may also be prepared by slowly adding aniline to a sulphurous acid solution of formaldehyde and gently heating the mixture on the water-bath.

Neutral propylidenedianiline hydrogen sulphite,

$$CH_2Me\cdot CH(NHPh)_2,H_2SO_3,$$

produced by shaking together propaldehyde and a sulphurous acid solution of aniline containing excess of the base, crystallises in snow-white prisms and decomposes at 89°.

Propylideneaniline sodium hydrogen sulphite, $CH_2Me\cdot CH{:}NPh,H_2SO_3$, prepared by adding aniline to a solution of propaldehyde in sulphurous acid, crystallises from the mixture, after concentration under diminished pressure, in silky, slender needles; it is readily decomposed on boiling with water.

Trichlorethylideneaniline hydrogen sulphite,  $CCl_3\cdot CH{<}\begin{matrix}NH_2Ph\\SO_2\end{matrix}{>}O$, results from the interaction of aniline dissolved in excess of sulphurous acid and chloral or freshly prepared solutions of the aldehyde; it separates in thin, monoclinic plates and melts at 93°. The compound may be crystallised from hot water without alteration, but is instantly decomposed by sodium carbonate solution and becomes yellow on exposure to the air (compare Boessneck, Abstr., 1888, 942).

Hydrated trichloroethylidenedianiline hydrogen sulphite,

$$CCl_3\cdot CH(NHPh)\cdot SO_2\cdot O\cdot NH_3Ph,$$

slowly separates from an aqueous solution containing aniline, chloral hydrate, and excess of sulphurous acid; it can be crystallised from water and is perfectly stable in the atmosphere; it forms long needles melting at 165° and dissolves in sodium carbonate solution without decomposition.

i-*Butylidenedianiline anhydrosulphite*, $C_3H_7{\cdot}CH(NHPh)_2{\cdot}SO_2$, obtained either by adding *i*-butaldehyde to an aniline solution in excess of sulphurous acid or by treating the hydrogen sulphite compound of *i*-butaldehyde with aniline, crystallises in sparingly soluble, white needles and melts at 126—127°.

i-*Valerylidenedianiline anhydrosulphite*, $C_4H_9{\cdot}CH(NHPh)_2{\cdot}SO_2$, prepared like the preceding compounds in aqueous solutions and also by passing sulphur dioxide into an ethereal solution of *i*-valerylideneaniline dissolved in ether, separates as a crystalline powder melting at 128—129°.

Heptylidenedianiline anhydrosulphite is obtained in small needles which obstinately retain the last traces of moisture, and when perfectly dry melt at 107—108°. The compound can be crystallised from water or alcohol, but is decomposed with its generators by sodium carbonate solution. The aniline anhydro-base of valeraldehyde and œnanthaldehyde do not combine with sodium hydrogen sulphite; on the other hand, the sodium hydrogen sulphite derivatives of these aldehydes are decomposed by aniline, yielding the corresponding anhydrosulphites.

Benzylidenedianiline anhydrosulphite, $CHPh(NHPh)_2{\cdot}SO_2$ (compare Michaelis, Abstr., 1891, 716), produced either by adding benzaldehyde to a strongly acid solution of aniline in sulphurous acid or by passing sulphur dioxide into a solution of benzylideneaniline in dry ether, crystallises in aggregates of needles and melts at 125°; it is immediately decomposed by sodium carbonate solution, and when heated with water changes into a *compound*, $C_{19}H_{18}N_2,SO_2,\frac{1}{2}H_2O$, which crystallises in flattened needles and melts and decomposes at 132—135°.

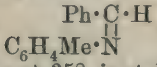
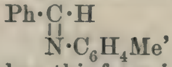
m-*Nitrobenzylidenedianiline anhydrosulphite*,

$$NO_2{\cdot}C_6H_4{\cdot}CH(NHPh)_2,SO_2,$$

and m-*nitrobenzylideneaniline hydrogen sulphite*,

$$NO_2{\cdot}C_6H_4{\cdot}CH{:}NPh,H_2SO_3,$$

are produced simultaneously by adding an alcoholic solution of *m*-nitrobenzaldehyde to aniline dissolved in sulphurous acid; the former is soluble in alcohol and crystallises in yellow needles and melts at 128°, the latter is insoluble in alcohol and crystallises from water in colourless leaflets melting at 177°. The yellow compound, when dissolved in alcohol and treated with sulphurous acid, is converted into the white sulphite, the converse change being effected by the action of heat on the latter substance. The *compound*, $OH{\cdot}C_6H_4{\cdot}CH{:}NPh,H_2SO_3$, melts at 128°, and is formed by adding salicylaldehyde to an aqueous aniline sulphite solution; it is decomposed by sodium carbonate and also by hot water or alcohol. G. T. M.

Condensation Products of Aldehydes and Amines. By Arthur Hantzsch and Otto Schwab (*Ber.*, 1901, 34, 822—839).—When *p*-toluidine is warmed with benzaldehyde (1 mol.), a yellowish oil is obtained which, after cooling, may behave in four different ways. (1) It rapidly forms a crystalline mass melting at 35°; (2) it partially solidifies, the crystals, after being drained, melting below 35°; the residual oil only deposits crystals after several days, and these melt between 28° and 33°; (3) the product remains liquid at the ordinary temperature, even after the addition of a crystal of the substance melting at 35°; when cooled, it solidifies at 11° to a mass melting at 12·5°, but after several days it deposits crystals melting at 35°, and after several months becomes completely solid and then melts at 35°; (4) the product is liquid at the ordinary temperature, but very gradually solidifies on adding a crystal of the compound melting at 35°. These facts indicate the existence of two stereoisomeric forms of *benzylidene*-p-*toluidine*,  $\begin{array}{c}\mathrm{Ph\cdot C\cdot H}\\ \|\\ \mathrm{C_6H_4Me\cdot N}\end{array}$ and  $\begin{array}{c}\mathrm{Ph\cdot C\cdot H}\\ \|\\ \mathrm{N\cdot C_6H_4Me}\end{array}$, only one of which, that melting at 35°, is stable; when this form is heated at the melting temperature for several minutes, it melts, after solidification, at temperatures varying between 12° and 33°. The original melting point is, however, regained when the solidified product is kept for some time at the ordinary temperature.

Benzylideneaniline shows a somewhat similar behaviour; it melts at 48°, and after solidifying remelts at 54°, whilst very varying melting points are attributed to it by other authors. The following compounds apparently exist in only one form; the melting points are given in brackets. p-*Chlorobenzylideneaniline*, $C_6H_4Cl\cdot CH{:}NPh$, white scales (66°); p-*chlorobenzylidene*-p-*chloroaniline*, yellowish-white needles (111°); o-*chlorobenzylidene*-p-*chloroaniline*, white crystals (68°); m-*nitrobenzylidene*-p-*chloroaniline*, yellowish crystals (81°); the *hydrochloride* melting at 185°; p-*nitrobenzylidene*-p-*chloroaniline*, yellow needles (128°); *benzylidene*-p-*anisidine*, white leaflets (142°); o-*hydroxybenzylidene*-p-*bromoaniline*, lustrous, yellow leaflets (112°); p-*methoxybenzylidene*-p-*anisidine*, white, lustrous leaflets (142°).

Benzylidene-p-*chloroaniline*, $CHPh{:}N\cdot C_6H_4Cl$, crystallises from alcohol in beautiful, white leaflets, melts at 62°, and yields a white, crystalline *hydrochloride*; this melts and decomposes at 194°, is converted by moist air into benzaldehyde and *p*-chloroaniline hydrochloride, and, with aqueous sodium carbonate below 0° yields *benzaldehyde*-p-*chloroaniline*, $OH\cdot CHPh\cdot C_6H_4Cl$, which melts at about 120° when rapidly heated, and is thereby converted, with loss of $1H_2O$, into benzylidene-*p*-chloroaniline. *Benzylidene*-p-*bromoaniline* crystallises from alcohol in white leaflets, melts at 67°, and yields a *hydrochloride* melting and decomposing at 195°; *benzaldehyde*-p-*bromoaniline*, $OH\cdot CHPh\cdot C_6H_4Br$, melts at about 120°, loses $1H_2O$, and subsequently melts at 67°. The hydrochlorides of the following compounds, when decomposed by aqueous sodium carbonate, regenerate their bases. 2 : 4 : 6-*Trimethylbenzylideneaniline* melts at 56°, and 2 : 4 : 6-*trimethylbenzylidene-ψ-cumidine* at 82° (the *hydrochloride* decomposes at 212°); 2 : 4 : 6-*trimethylbenzylidene*-p-*chloroaniline* crystallises from alcohol in long needles, the yellow *hydrochloride* decomposing at 183°. o-*Hydroxybenzylideneaniline* forms yellow crystals and melts at 51°.

Benzaldehyde and *p*-nitroaniline, after long heating at 120°, yield *benzylidene*-p-*nitroaniline* melting at 118°, but at the ordinary temperature, in absolute alcoholic ethereal solution, 2 mols. of the base combine with 1 mol. of the aldehyde to form *benzylidenebis-*p*-nitroaniline*, $CHPh(NH\cdot C_6H_4\cdot NO_2)_2$, which, obtained in an impure state, was considered by von Miller and Rohde (Abstr., 1892, 1189) to be the compound $OH\cdot CHPh\cdot NH\cdot C_6H_4\cdot NO_2$; it forms yellow crystals, melts at 85°, and is decomposed by heating, either alone or with benzene or water, into benzylidene-*p*-nitroaniline and *p*-nitroaniline.

Benzylidenebisaminothiazole, $CHPh(C_3H_3N_2S)_2$, obtained from benzaldehyde and aminothiazole (2 mols.), melts indefinitely when slowly heated, but instantaneously when plunged into a bath heated to 138°; decomposition here occurs into benzylideneaminothiazole and aminothiazole, but recombination occurs on cooling (compare Hantzsch and Witz, this vol., i, 401).

Benzylidene-*p*-toluidine combines with methyl iodide at the ordinary temperature to form the crystalline *methiodide*, $CHPh\colon NMeI\cdot C_6H_4Me$, which is decomposed by water or moist air, yielding benzaldehyde, and by aqueous sodium hydroxide yielding *p*-toluidine, not methyl-*p*-toluidine. *Benzylidene-*p*-toluidine ethiodide* melts and decomposes at 170°; the methiodide and ethiodide of benzylideneaniline are crystalline, but rapidly decompose, yielding complex products; the existence of Borodin's bases of the type $CHPh\colon NPhMe\cdot OH$ seems doubtful (compare *Annalen*, 1859, **111**, 254).

Ethylidenebenzylamine, from acetaldehyde and benzylamine, boils at 145° and resinifies with methyl iodide; benzylidene-ethylamine (b. p. 187—188°) similarly does not yield a methiodide.

[Supplement by PAUL JACOBSON and A. STEINBRENCK (compare *Diss., Heidelberg*, 1896)].—*o-Hydroxybenzylidene-*o*-toluidine* crystallises from light petroleum in needles, melts at 47—48°, and yields with iodine an unstable, violet, additive compound, $C_{14}H_{13}ONI_4$. o-*Hydroxybenzylidene-*o*-bromoaniline* forms yellow prisms melting at 85—86°. *Benzylidene* o-*phenetidine* boils at 215—216° under 20 mm. pressure; o-*hydroxybenzylidene-*o*-phenetidine* boils at 228—229° under 17 mm. pressure.

W. A. D.

Condensation of *o*-Hydroxybenzylideneaniline. By OTTO SCHWAB (*Ber.*, 1901, **34**, 839—840).—Although benzylideneaniline fails to undergo the benzoin condensation with potassium cyanide (von Miller and Plöchl, *Ber.*, 1896, 1730, and 1898, 2699), *o*-hydroxybenzylideneaniline readily yields the *compound*

$$OH\cdot C_6H_4\cdot CH(NHPh)\cdot C(NPh)\cdot C_6H_4\cdot OH,$$

at the ordinary temperature; it separates from alcohol in lustrous, yellow crystals and melts at 155°.

W. A. D.

Preparation of Morpholine. By WILHELM MARCKWALD and M. CHAIN (*Ber.*, 1901, **34**, 1157—1159. Compare Knorr, Abstr., 1898, i, 601; 1899, i, 784).—p-*Tolylsulphonedi-β-naphthoxyethylamide*, $C_7H_7\cdot SO_2\cdot N(CH_2\cdot O\cdot C_{10}H_7)_2$, obtained from *p*-tolylsulphonamide (1 mol.), β-naphthyl bromoethyl ether (2 mols.), and alcoholic potash, crystallises from acetic acid, melts at 130°, and is only sparingly soluble in alcohol. When hydrolysed with mineral acids at 170—180°, it is quantitatively converted into toluene, sulphuric acid, β-naphthol, and morpholine.

Contrary to Weddige's statement (Abstr., 1881, 1137), a considerable amount of primary base, phenoxyethylamine, is obtained by the action of ammonia on phenyl bromoethyl ether (bromophenetole). The *hydrobromide* melts at 192—193°.

J. J. S.

Chloro-derivatives of *s*-Diphenylcarbamide and their Reactions. By FREDERICK D. CHATTAWAY and KENNEDY J. P. ORTON (*Ber.*, 1901, **34**, 1073—1078).—*s*-Diphenylcarbamide is converted by hypochlorous acid into a diphenyldichlorocarbamide, the iminohydrogen atom being replaced by chlorine. This substance readily undergoes molecular change, producing *s*-di-*p*-chlorophenylcarbamide, which, in its turn, can be converted into a dichloroamino-derivative, which passes by intramolecular change into *s*-di-2 : 4-dichlorophenylcarbamide. This series of changes can again be repeated, the final product being *s*-di-2 : 4 : 6-trichlorophenyldichlorocarbamide.

s-Diphenyldichlorocarbamide, $CO(NPhCl)_2$, is obtained by the action of alkaline potassium hypochlorite solution on diphenylcarbamide, and crystallises in large, colourless prisms, which, when rapidly heated, melt at 101—102°, forming a colourless liquid, which then becomes dark coloured and explodes. When it is heated in acetic acid solution, molecular change takes place, *s*-di-*p*-chlorophenylcarbamide being produced along with small amounts of two isomeric dichlorophenylcarbamides. The main product has previously been described by Beilstein and Kurbatoff (*Annalen*, 1875, **176**, 46), and is best prepared by heating carbamide with *p*-chloroaniline. When it is treated with bleaching powder and potassium hydrogen carbonate, it yields s-*di*-p-*chlorophenylmonochlorocarbamide*, $C_6H_4Cl\cdot NH\cdot CO\cdot NCl\cdot C_6H_4Cl$, which crystallises in bundles of needles, or in long, thin plates, which melt at about 132° when rapidly heated, but solidify again at a somewhat higher temperature. s-*Di*-p-*chlorophenyldichlorocarbamide*, $CO(NCl\cdot C_6H_4Cl)_2$, is produced along with the foregoing compound when chlorophenylcarbamide is treated with bleaching powder and acetic acid, and forms short, colourless prisms, which melt and partially decompose at 171—173° when rapidly heated. On treatment with acetic acid at 100°, it partially decomposes and partially undergoes molecular change, producing s-*di*-2 : 4-*dichlorophenylcarbamide*, $CO(NH\cdot C_6H_3Cl_2)_2$, which can also be prepared by heating carbamide with 2 : 4-dichloroaniline, and crystallises in thin, colourless needles melting at 273°, with partial decomposition when rapidly heated. When it is treated with chlorine in presence of acetic acid and potassium acetate, it yields s-*di*-2 : 4-*dichlorophenyldichlorocarbamide*, $CO(NCl\cdot C_6H_3Cl_2)_2$, which crystallises in strongly refractive prisms, and melts and partially decomposes at about 160° when rapidly heated. When heated with acetic acid, it yields s-*di*-2 : 4 : 6-*trichlorophenylcarbamide*, $CO(NH\cdot C_6H_2Cl_3)_2$, which crystallises in very thin needles melting with decomposition at 320—325° when rapidly heated. Alcoholic ammonia produces carbamide and 2 : 4 : 6-trichloroaniline. Bleaching powder and acetic acid convert it into s-*di*-2 : 4 : 6-*trichlorophenyldichlorocarbamide*, $CO(NCl\cdot C_6H_2Cl_3)_2$, which crystallises in strongly refractive, four-sided prisms terminated by dome faces, and melts and decomposes at about 190° when rapidly heated.

A. H.

Bromination of s-Diphenylcarbamide. By FREDERICK D. CHATTAWAY and KENNEDY J. P. ORTON (*Ber.*, 1901, **34**, 1078—1081. Compare preceding abstract).—Bromine acts on s-diphenylcarbamide in a similar manner to chlorine, but the intermediate products have not been isolated. s-*Di*-p-*bromophenylcarbamide*, $CO(NH\cdot C_6H_4Br)_2$, is obtained by the direct action of bromine on the carbamide in presence of acetic acid and sodium acetate, and crystallises in thin prisms which melt and decompose at about 330° when rapidly heated. On heating with alcoholic ammonia, it yields *p*-bromoaniline and carbamide. The compound described under this name by Otto (*Ber.*, 1869, **2**, 408), and by Sarauw (*Ber.*, 1882, **15**, 42), is stated by them to sublime at 225° without previously melting.

s-*Di*-2 : 4-*dibromophenylcarbamide*, $CO(NH\cdot C_6H_3Br_2)_2$, is obtained by boiling the carbamide with excess of bromine in presence of acetic acid and sodium acetate. It crystallises in colourless, silky needles, and melts and partially decomposes at 281° when rapidly heated. Alcoholic ammonia converts it into 2 : 4-dibromoaniline and carbamide.

s-*Di*-2 : 4 : 6-*tribromophenylcarbamide*, $CO(NH\cdot C_6H_2Br_3)_2$, is obtained when a mixture of diphenylcarbamide, bromine, acetic acid, and sodium acetate is heated at 130—135°. It crystallises in colourless, hair-like needles, which melt and decompose at about 320°. Alcoholic ammonia converts it into carbamide and 2 : 4 : 6-tribromoaniline. A. H.

Electrolysis of Phenol in presence of Hydrogen Haloids. By HERIBERT ZEHRLANT (*Zeit. Elektrochem.*, 1901, **7**, 501—505).—In presence of hydrochloric acid, phenol is oxidised at the anode and not chlorinated, owing to the facts that oxygen is liberated at a lower potential than chlorine and that phenol acts as a depolariser for anodic oxygen. In presence of *N* hydrobromic acid, the same thing occurs, but when 4 *N* hydrobromic acid is used, from which bromine ions are discharged at a lower potential, a certain amount of brominated product is obtained. In presence of hydriodic acid, iodine is liberated without acting on the phenol. T. E.

Some Derivatives of Phenyl Ether. By CARL HAEUSSERMANN and AUG. MÜLLER (*Ber.*, 1901, **34**, 1069. Compare Abstr., 1896, i, 533).—The potassium derivatives of the cresols react with *o*- and *p*-chloronitrobenzene in a similar manner to potassium phenoxide, whereas those of the naphthols under similar circumstances simply act as reducing agents. *Quinol* p-*nitrodiphenyl ether*, is obtained by heating the potassium compound of *p*-hydroxyphenyl ether with *p*-chloronitrobenzene, and crystallises in lustrous plates melting at 91—92·5°. On reduction in alcoholic solution with tin and hydrochloric acid, it yields *quinol* p-*aminodiphenyl ether*, which crystallises in almost colourless prisms melting at 83—84·5°. The *hydrochloride* is sparingly soluble in cold water and crystallises in silvery scales melting at 210°, whilst the *sulphate* is insoluble in boiling water. The base can be converted into a diazo-compound which yields reddish azo-compounds. When the base is treated in alcoholic solution with nitrous acid and the liquid boiled, *quinol diphenyl ether* is produced, which crystallises in white needles melting at 74—75°, can be distilled at the ordinary pressure and is not affected by acetic anhydride. A. H.

Action of Iodine and Yellow Mercuric Oxide on Anethole, Estragole, Safrole, &c. By J. BOUGAULT (*Bull. Soc. Chim.*, 1901, [iii], **25**, 444—446. Compare Abstr., 1900, i, 494, 641).—The action of iodine and mercuric oxide on cyclic compounds containing a propenylic side chain takes place in two stages, the first stage consisting in the fixation of HIO with the formation of a compound, $R\cdot CHI\cdot CHMe\cdot OH$, which then undergoes transformation into the aldehyde, $R\cdot CHMe\cdot CHO$, with elimination of HI. These intermediate compounds may be isolated by employing a limited amount of mercuric oxide, or by replacing the latter by mercuric chloride; they are more or less unstable, uncrystallisable substances which are readily reduced by zinc and acetic acid and are decomposed on exposure to air and light with liberation of iodine. N. L.

New Synthesis of Aromatic Sulphones. By FRITZ ULLMANN and G. PASDERMADJIAN (*Ber.*, 1901, **34**, 1150—1156).—Aromatic sulphinic acids readily react with alcoholic solutions of halogen derivatives of aromatic nitro-compounds, yielding diphenylsulphone derivatives. In certain cases, for example, with *o*- and *p*-chloronitrobenzene, chloronitrobenzoic acid, &c., it is necessary to work under increased pressure and in presence of sodium acetate.

2 : 4 : 6-*Trinitrodiphenylsulphone*, $C_6H_2(NO_2)_3\cdot SO_2Ph$, crystallises in pale yellow, well developed rhombohedra melting at 233° (corr.), and insoluble in alcohol or ether. 2 : 4-*Dinitrodiphenylsulphone*, $C_6H_3(NO_2)_2\cdot SO_2Ph$, crystallises in colourless needles, melts at 157°, and dissolves in hot benzene or acetic acid. When reduced with stannous chloride and hydrochloric acid in the presence of alcohol, it yields 2 : 4-*diaminodiphenylsulphone*, which crystallises in colourless, hexagonal needles melting at 188°, and insoluble in water or ether; the *diacetyl* derivative crystallises in needles melting at 197°. 2-*Nitrodiphenylsulphone*, $NO_2\cdot C_6H_4\cdot SO_2Ph$, crystallises in colourless, feathery needles melting at 147·5°, and readily soluble in most organic solvents. 2-*Aminodiphenylsulphone* crystallises in glistening plates melting at 122°, and yields an *acetyl* derivative melting at 132°. 2-*Hydroxydiphenylsulphone*, obtained from the amino-compound, crystallises in small, hexagonal prisms melting at 82°, and readily soluble in most organic solvents or in alkalis. A small amount of diphenylsulphone is also obtained as a bye-product.

4-*Nitrodiphenylsulphone* crystallises in colourless needles melting at 143°, and readily soluble in benzene, alcohol, or acetic acid. 4-*Aminodiphenylsulphone* crystallises in needles melting at 176°, and yields an *acetyl* derivative crystallising in prisms and melting at 195°.

2 : 6-*Dinitrodiphenylsulphone-4-carboxylic acid*,

$$CO_2H\cdot C_6H_2(NO_2)_2\cdot SO_2Ph,$$

crystallises from hot water in long, colourless needles which darken at 220° and decompose and melt at 240°.

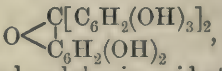
2-*Nitrodiphenylsulphone-4-carboxylic acid* forms yellowish crystals melting at 255—260°, and readily soluble in alcohol or acetic acid. 2-*Aminodiphenylsulphone-4-carboxylic acid* melts at 270—275°.

J. J. S.

So-called Dinaphthylene Glycol Anhydride. By ROBERT FOSSE (*Compt. rend.*, 1901, **132**, 1127—1129. Compare this vol., i, 322).—The compound described by Rousseau (Abstr., 1882, 1299) as the anhydride of dinaphthylene glycol is identical with dinaphthaxanthen.

C. H. B.

Derivatives of Eupittone [Hexamethoxyaurin]. By CARL LIEBERMANN and FRITZ WIEDERMANN (*Ber.*, 1901, **34**, 1031—1040).—Eupittone is shown by Zeisel's method to contain six methoxy-groups. The *hydrochloride*, $C_{25}H_{26}O_9,HCl,C_2H_6O$, is obtained by treating eupittone with alcoholic hydrochloric acid. The alcohol of crystallisation is only lost after remaining for 11 days in a desiccator, leaving the very hygroscopic hydrochloride.

Eupittone black (*hexahydroxyaurin*),  $O<\begin{matrix}C[C_6H_2(OH)_3]_2\\ |\\ C_6H_2(OH)_2\end{matrix}$, is prepared by heating eupittone with concentrated sulphuric acid at 110°, when the colour changes from red to blue. It is an amorphous, lustreless powder, soluble in boiling water or alcohol, and with mordants forms a fast black dye. From the alcoholic solution, hydrochloric acid precipitates a *hydrochloride*, $C_{19}H_{14}O_9,HCl,C_2H_6O$, as a deep blue powder. Partial removal of the methyl groups was not found to be possible.

Hexahydroxyleucaniline hydriodide, $CH[C_6H_2(OH)_2{\cdot}NH_3I]_3,2H_2O$, prepared by the action of hydriodic acid and acetic anhydride on eupittone, forms silky, lustrous needles. Concentrated hydrochloric acid converts the hydriodide into a *hydrochloride* crystallising with H_2O.

Oxidation of a solution in acetic acid transforms the leuco-base into hexahydroxyrosaniline, a brilliant blue dye. *Nona-acetylhexahydroxyleucaniline* forms colourless needles melting at 172—173°.

Formylhexamethoxydimethylleucaniline,

$$CHO{\cdot}NH{\cdot}C_6H_2(OMe)_2{\cdot}CH[C_6H_2(OMe)_2{\cdot}NHMe]_2,$$

is prepared by the action of methylamine on eupittone, and forms transparent, colourless prisms melting at 187° and soluble in dilute acids. Oxidation of the acid solution converts it into the blue colour-base.

Leuco-eupittone (*hexamethoxyleucaurin*), $CH{\cdot}[C_6H_2(OMe)_2{\cdot}OH]_3$, obtained by the reduction of the sodium salt of eupittone by zinc dust, crystallises in colourless needles melting and decomposing at 198°. It dissolves in alkalis to a colourless solution, which on boiling becomes blue, with the formation of eupittone. The *triacetate* forms colourless needles melting at 236°.

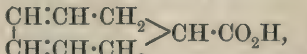
K. J. P. O.

Eupittone and Pittakal. By CARL LIEBERMANN (*Ber.*, 1901, **34**, 1026—1030).—Pittakal, discovered by von Reichenbach (*J. Chem. Physik.*, 1833, **68**, 1) is, shown to be a salt of eupittone (hexamethoxyaurin). Reichenbach described it erroneously as a colouring matter capable of mordanting with oxides, with the production of a fast dye, which resembled indigo. The author shows that this is not the case, as the absence of two hydroxyl groups in the ortho-position to one another would indicate. K. J. P. O.

2 : 3-Diaminobenzoic Acid and its Compounds with the Sugars. By BRUNO SCHILLING (*Ber.*, 1901, **34**, 902—907).—The condensation compounds of sugars with 2 : 3-diaminobenzoic acid have been investigated. The compounds from dextrose and maltose (Griess and Harrow, Abstr., 1888, 267) are probably derivatives of benziminazole, since, when oxidised with potassium permanganate, they yield the monocarboxylic acid of this substance. The *compound* from lactose and 2 : 3-diaminobenzoic acid crystallises in small pyramids and melts at 206°. Owing to the difficulty in purifying these condensation products, they are not suited for the identification of the sugars.

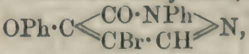
R. H. P.

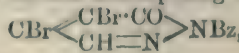
ψ-Phenylacetic Acid or Norcaradienecarboxylic Acid. By WILHELM BRAREN and EDUARD BUCHNER (*Ber.*, 1901, **34**, 982—997. Compare Abstr., 1900, i, 292, and this vol., i, 85).—Ethyl norcaradienecarboxylate (ethyl ψ-phenylacetate) boiling at 108° under 13 mm. pressure as obtained by fractionation, contains ethyl fumarate and also ethyl β-*cyclo*heptatrienecarboxylate, as the latter is obtained when the ψ-phenylacetate is heated at 150°. On treatment with concentrated sulphuric acid, the ester gives a cherry-red coloration which gradually changes to violet and then to indigo blue. Little or no condensation takes place when methyl diazoacetate is employed in place of the ethyl ester. The pure acid is best obtained by converting the ethyl ester into the amide; the yield of amide is not good even when the ester is left for several weeks in closed vessels with aqueous ammonia saturated at 0°; the chief bye-product is β-cyclo*heptatrienecarbonylamide* which melts at 157°.

$\Delta^{2\cdot4}$-Norcaradiene-7-carboxylic acid, 
$\begin{matrix}\mathrm{CH{:}CH\cdot CH_2}\\ \mathrm{CH{:}CH\cdot CH_2}\end{matrix}\!\!>\mathrm{CH\cdot CO_2H}$, is obtained when the amide is heated with 30 per cent. sulphuric acid and at the same time distilled in steam. It is an oil which solidifies at about −18°, and is stable in the air; the *sodium*, *barium*, and *magnesium* salts are readily soluble, the *silver*, *cupric*, and *mercurous* salts only sparingly. The *anilide* melts at 141—142°, the *dibromide* melts and decomposes at 159—160°, is readily oxidised by permanganate, and when treated with zinc dust and acetic acid is reconverted into the original acid. The *tetrabromide*, 2 : 3 : 4 : 5-*tetrabromonorcarane-7-carboxylic acid*, $C_7H_7Br_4\cdot CO_2H$, melts and decomposes at 233—235°, is not oxidised by permanganate, gives no coloration with concentrated sulphuric acid, and loses its four atoms of bromine when treated with zinc dust and acetic acid.

The chief products formed when norcaradienecarboxylic acid is oxidised with cold acid permanganate are phthalic, benzoic, and *trans*-1 : 2 : 3-trimethylenetricarboxylic acids. J. J. S.

Mixed Anhydrides. By ÉMILE SEVERIN (*Bull. Soc. Chim.*, 1901, [iii], **25**, 500—510. Compare Abstr., 1900, i, 296 and 598).—According to Béhal (Abstr., 1900, i, 8), when the mixed anhydride of acetic acid and another acid is treated with alcohol, ammonia, phenylhydrazine, or hydrochloric acid, the ester, amide, phenylhydrazide, or chloride of acetic acid is formed, whilst the other acid of higher molecular weight is set free. Since a behaviour exactly the reverse of this was observed with the mixed anhydrides studied by the author, a quantity of acetic 3 : 6-dichloro-2-dimethylaminobenzoylbenzoic anhydride was prepared and carefully purified for detailed examination. The discrepancy between Béhal's and the author's results might readily be explained by the assumption that the author's anhydride was the true anhydride of the acid of higher mol. weight, but the results of analysis, the production of acetic anhydride on distillation under diminished pressure, and other facts, conclusively prove the substance to be a mixed acetic anhydride. The action of ammonia on the anhydride leads to the formation of 3 : 6-*dichloro-2-dimethylaminobenzoylbenzamide*, $NMe_2{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_2Cl_2{\cdot}CO{\cdot}NH_2$, which crystallises in thin, white scales melting at 220°. The corresponding *phenylhydrazide*, obtained by the action of phenylhydrazine on the mixed anhydride, crystallises in white scales melting at 196°. The acid *chloride* is produced in small quantity by the action of hydrochloric acid on the mixed anhydride; it crystallises with difficulty. The formation of the methyl and ethyl esters of 3 : 6-dichloro-2-dimethylaminobenzoylbenzoic acid has already been described (Abstr., 1900, i, 296). From these results, it appears that the introduction of negative groups into the benzene nucleus causes a transference of the activity of the molecule to the radicle of higher molecular weight. N. L.

Aliphatic-γ- and Aromatic-*o*-aldehydo-acids. By AUGUSTIN BISTRZYCKI and C. HERBST (*Ber.*, 1901, **34**, 1010—1021).—The authors point out that most of the reactions described by Anschütz (*Annalen*, 1887, **239**, 177), Hill and Cornelison (Abstr., 1894, i, 319, 320), and Hill and Dunlap (*ibid.*, 1897, i, 571), in favour of the lactone formula for mucobromic acid, can be just as readily explained by the old aldehydo-formula, provided a direct addition of the reagent to the aldehydo-group is assumed, and then subsequent elimination of water. Most of the reactions described in the present paper favour the aldehydo-formula. Mucobromic acid phenylhydrazone (Abstr., 1899, i, 392) crystallises in yellow needles decomposing at 105—106°. *Mucophenoxybromic acid phenylhydrazone*, $CO_2H{\cdot}C(OPh){:}CBr{\cdot}CH{:}N{\cdot}NHPh$, crystallises in deep yellow needles melting and decomposing at 157°, and insoluble in benzene; when boiled with acetic anhydride, it yields 4-*bromo-5-phenoxy-1-phenylpyridazone*,  $OPh{\cdot}C{<}\begin{matrix}CO{\cdot}NPh\\CBr{\cdot}CH\end{matrix}{>}N$, which crystallises in yellow needles melting at 115°. *Mucophenoxybromic acid semicarbazone*, $CO_2H{\cdot}C(OPh){:}CBr{\cdot}CH{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$, melts at 195°, and is only sparingly soluble in the usual solvents. *Mucobromic acid semicarbazone* crystallises in colourless, microscopic prisms melting at 215°; when crystallised from acetic acid, it yields 4 : 5-dibromopyridazone melting at 218°, not at 224° as previously stated.

Mucobromic acid benzoylhydrazone, $CO_2H{\cdot}CBr{:}CBr{\cdot}CH{:}N{\cdot}NHBz$, crystallises in felted needles decomposing at 140—141°. 4 : 5-*Dibromo-1-benzoylpyridazone*,  $CBr{<}\begin{matrix}CBr{\cdot}CO\\CH{=}N\end{matrix}{>}NBz$, obtained by the action of phosphoryl chloride and then water on the benzoylhydrazone, crystallises in colourless prisms decomposing at 187°. *Mucophenoxybromic acid benzoylhydrazone* crystallises from acetone in flat prisms melting and decomposing at 146°, and practically insoluble in the usual solvents. So far, it has not been converted into a pyridazone.

Opianic acid benzoylhydrazone, $C_6H_2(OMe)_2(CO_2H)\cdot CH\colon N\cdot NHBz$ $[(OMe)_2 : CO_2H : CH = 5 : 6 : 1 : 2]$, forms microscopic crystals melting and decomposing at 227°. *Phthalaldehydic acid benzoylhydrazone*, $CO_2H\cdot C_6H_4\cdot CH\colon N\cdot NHBz$, crystallises in colourless prisms or plates melting and decomposing at 189°.

Opianic acid N-*phenyloxime*, $C_6H_2(OMe)_2(CO_2H)\cdot CH{<}\begin{matrix}NPh\\ |\\ O\end{matrix}$, obtained by boiling a solution of opianic acid and phenylhydroxylamine in absolute alcohol, crystallises in flat needles melting at 174°, and insoluble in benzene or light petroleum, but readily soluble in sodium carbonate solution. Opianic acid and *p*-aminophenol react, forming *opianylidene*-p-*hydroxyaniline*, $CO_2H\cdot C_6H_2(OMe)_2\cdot CH\colon N\cdot C_6H_4\cdot OH$, which crystallises in glistening plates melting at 223°, and only sparingly soluble in the usual solvents; as it is readily soluble in sodium carbonate solution, it cannot have a lactonic constitution (compare Liebermann, Abstr., 1896, i, 132). *Bromo-opianic acid* N-*phenyloxime*, forms glistening prisms. *Phthalaldehydic acid* N-*phenyloxime* forms colourless needles decomposing at 125° after drying at 80°. Both mucobromic and mucophenoxybromic acid react with phenylhydroxylamine, but the products are oily.

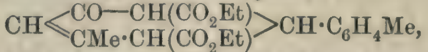
Mucobromic acid ethylenediamine, $C_6H_8O_2N_2Br_2$, decomposes at 117°, and is insoluble in organic solvents, but dissolves in sodium carbonate solution. Mucobromoamide, when treated with concentrated sulphuric acid, yields an *anhydride*, $\begin{matrix}CBr\cdot CO\\ \|\\ CBr\cdot CH\end{matrix}{\geqslant}N$, melting at 153°. J. J. S.

isoAlantolactone, a Constituent of the Root of Inula Helenium. By JULIUS SPRINZ (*Arch. Pharm.*, 1901, **239**, 201—213).—This paper is almost identical with one already published (this vol., i, 325). *iso*Alantolic acid melts at the same temperature as its lactone, and its calcium salt crystallises from a hot dilute solution with $2\frac{1}{2}H_2O$.
C. F. B.

Ethyl *p*-Methylbenzylideneacetoacetate. By BERNHARD FLÜRSCHEIM (*Ber.*, 1901, **34**, 787—791. Compare Knoevenagel, Abstr., 1895, i, 48, &c.).—When *p*-tolualdehyde is mixed with ethyl acetoacetate and a little diethylamine, the mixture heated to 40° and allowed to remain for several weeks, *ethyl*-p-*methylbenzylidenebisacetoacetate*,

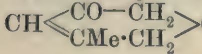
$$C_6H_4Me\cdot CH(CHAc\cdot CO_2Et)_2,$$

melting at 132·5° is formed. In one experiment, when but a little diethylamine was added at first, *ethyl* p-*methylbenzylideneacetoacetate*, $C_6H_4Me\cdot CH\colon CAc\cdot CO_2Et$, melting at 74°, was obtained quite unexpectedly. By heating this substance with ethyl β-aminocrotonate and a little alcohol at 100°, *ethyl* 4-p-*tolyl*-2 : 6-*dimethyldihydropyridine*-3 : 5-*dicarboxylate*, $NH{<}\begin{matrix}CMe\colon C(CO_2Et)\\ CMe\colon C(CO_2Et)\end{matrix}{>}CH\cdot C_6H_4Me$, melting at 138°, is obtained. When the bisacetoacetate is dissolved in absolute alcohol and the solution saturated with gaseous hydrogen chloride, *ethyl* 5-p-*tolyl*-3-*methyl*cyclo*hexenone*-4 : 6-*dicarboxylate*,



$$\mathrm{CH}<\begin{matrix}\mathrm{CO-CH(CO_2Et)}\\ \mathrm{CMe\cdot CH(CO_2Et)}\end{matrix}>\mathrm{CH\cdot C_6H_4Me},$$

melting at 84—85° is formed. When the bisacetoacetate is heated at 100° with aqueous potassium hydroxide, 5-p-*tolyl*-3-*methyl*cyclo*hexenone*,



$\mathrm{CH}<\begin{matrix}\mathrm{CO-CH_2}\\ \mathrm{CMe\cdot CH_2}\end{matrix}>\mathrm{CH\cdot C_6H_4Me}$, and β-p-*tolylglutaric acid*,

$$C_6H_4Me\cdot CH(CH_2\cdot CO_2H)_2,$$

are formed; the latter melts at 164—165°; the former melts at 42—43°, and boils at 198—202° under a pressure of 16 mm., whilst its *oxime* melts at 125—126°. When the potash solution is concentrated, more of the glutaric acid is obtained; when it is dilute, more of the hexenone; a liquid product boiling and decomposing at 70—80° is also obtained, possibly an unsaturated fatty acid. C. F. B.

Eugenolglycollic Acid [Eugenoxyacetic Acid]. By ROBERT CLAUSER (*Monatsh.*, 1901, **22**, 123—144).—It is shown that the eugenoxyacetic acid (m. p. 81°) obtained by previous investigators contained water of crystallisation ($1H_2O$). On drying in a vacuum or recrystallising from anhydrous solvents, the anhydrous acid melting at 100° is obtained. The *potassium* salt, $C_{12}H_{13}O_4K,\frac{1}{2}H_2O$, forms long needles; the *barium* salt crystallises in needles with $2H_2O$; the *zinc* and *copper* salts are crystalline precipitates, containing respectively 4 and $2H_2O$, whilst the *silver* salt is an anhydrous crystalline powder. The *methyl* ester forms colourless crystals melting at 43° and boiling at 161—164° under 19 mm. pressure. The *ethyl* ester forms large, white crystals melting at 36—37° and distilling at 200—205° under 19 mm. pressure. The *amide*, crystallises from water in needles melting at 110°. The *anilide* crystallises from petroleum in rectangular rhombic plates melting at 58°. The *phenylhydrazide*, forms slightly yellow plates melting at 113°.

On brominating eugenoxyacetic acid in chloroform solution, two substances are obtained. They are separated by crystallising from aqueous potassium carbonate, in which, when cold, only *dibromoeugenoxyacetic acid* is soluble, whilst the other *compound*, $C_{12}H_{13}Br_3O_5$ (?), which forms needles melting at 153—154°, crystallises out. The acid crystallises in needles melting at 93—94°; *methyl dibromoeugenoxyacetate* forms needles melting at 70°; the *amide*, obtained from the methyl ester or by brominating eugenoxyacetamide, crystallises in needles melting at 85°.

Diiodoeugenoxyacetic acid is obtained by the action of iodine on a chloroform solution of the acid in the form of very unstable crystals which decompose at 96°.

Nitroeugenoxyacetic acid is prepared by the carefully regulated action of nitric acid on eugenoxyacetic acid in acetic acid solution; it crystallises in rosettes of needles melting at 115—116°. With excess of nitric acid a strongly acid *dinitro*-compound,

$$C_3H_5\cdot C_6H(OH)(NO_2)_2\cdot O\cdot CH_2\cdot CO_2H,$$

is obtained as very insoluble yellow needles melting and decomposing at 154°. K. J. P. O.

Phenacyllævulic Acid and a new Carboxylic Acid, $C_{13}H_{13}O_2N$, of the Pyrrole Group. By EDUARD A. KEHRER (*Ber.*, 1901, **34**, 1263—1268. Compare Abstr., 1899, i, 568).—The *potassium, sodium, calcium, silver*, and *zinc* salts of phenacyllævulic acid are described. The *dioxime*, $C_{13}H_{16}O_4N_2$, melts at 144°. By heating with acetic acid and ammonium acetate, *β-5-phenylpyrrylpropionic acid*,

$$C_4NH_3Ph\cdot CH_2\cdot CH_2\cdot CO_2H,$$

is produced, which crystallises from chloroform or ether in hexagonal plates and melts at 140—141°; the silver and calcium salts are also described. T. M. L.

Le Royer's Dichlorophthalic Acid. By ÉMILE SEVERIN (*Bull. Soc. Chim.*, 1901, [iii], **25**, 499—500).—The dichlorophthalic acid previously studied by the author (Abstr., 1900, i, 296) and assumed, on Le Royer's authority, to be an *ortho*-derivative, has since been shown by Graebe (Abstr., 1900, i, 546) to be in reality the *para*-acid.

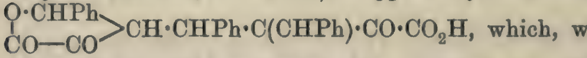
N. L.

***p*-Hydroxyhydratropic Acid.** By J. BOUGAULT (*Compt. rend.*, 1901, **132**, 976—978. Compare Abstr., 1900, i, 495, 548).—*p*-Hydroxyhydratropic acid, first obtained by Trinius (compare Abstr., 1885, 529), is readily prepared by digesting on the water-bath a mixture of *p*-methoxyhydratropic acid, iodine, red phosphorus, and concentrated hydriodic acid. It crystallises in colourless prisms melting at 130°, and readily dissolves in the ordinary organic solvents, 2·5 parts being soluble in 100 parts of water at 12°. The substance, when obtained by the preceding process, is a racemic compound, and may be split into its optical constituents by means of morphine, the salt of the lævorotatory acid with this alkaloid being less soluble in water than that of the dextrorotatory compound. *l-p*-Hydroxyhydratropic acid has $[\alpha]_D$ −71°. Saturated aqueous solutions of the acid yield precipitates with lead and mercurous acetates, but not with silver nitrate; ferric chloride develops a bluish-green coloration, which becomes brown on adding sodium hydroxide. The juice of *Russula delica* oxidises the acid developing a red coloration. The sodium, potassium, barium, calcium, and magnesium salts are very soluble; the zinc salt dissolves in less than 10 parts of cold water, whereas zinc *p*-hydrocoumarate requires for its solution 130 parts of this solvent. The *dibromide, diiodide*, and the *methyl* and *ethyl* esters of *p*-hydroxyhydratropic acid melt at 115°, 149°, 57°, and 68° respectively; they are prepared by methods identical with those employed in the case of the corresponding derivatives of *p*-hydrocoumaric (phloretic) acid, and the paper includes a table comparing the melting points of the two series. G. T. M.

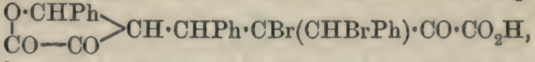
Occurrence of Quinic Acid. By EDMUND O. VON LIPPMANN (*Ber.*, 1901, **34**, 1159—1162).—A small amount of Hesse's quinide (*Annalen*, 1859, **110**, 335) has been isolated from the alcoholic extract of a powder deposited when beetroot leaves are dried at a moderate temperature. When hydrolysed with alkalis, it yields *i*-quinic acid; when an aqueous solution of this is left exposed to the atmosphere, fermentation begins, and *d*-quinic acid is left. It melts at 164°, and has $[\alpha]_D$ +44° at 20°.

A substance, *betitol*, $C_6H_{12}O_4$, has been isolated from beetroot extract after removal of the sugar; it crystallises in colourless prisms, melts at 224°, is readily soluble in water, has a dextorotatory power, and on oxidation yields quinone. J. J. S.

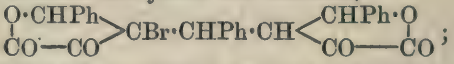
Condensation of Pyruvic Acid with Benzaldehyde. By EMIL ERLENMEYER, jun. (*Ber.*, 1901, **34**, 817—821. Compare Abstr., 1899, i, 601).—The gelatinous substance formed along with cinnamylformic acid by the action of benzaldehyde on pyruvic acid (Claisen and Claparède, Abstr., 1882, 520) is apparently the sodium salt of an *acid*,



$\left.\begin{array}{l}\text{O·CHPh}\\ \text{CO—CO}\end{array}\right>\text{CH·CHPh·C(CHPh)·CO·CO}_2\text{H}$, which, when liberated by hydrochloric acid, separates from alcohol in efflorescent crystals of the composition $3C_{27}H_{20}O_6,4C_2H_6O$, and on adding light petroleum is precipitated from its chloroform solution in lustrous needles melting at 208°; the *sodium* salt, $C_{27}H_{19}O_6Na,C_2H_6O$, crystallises from alcohol in long, colourless needles. The acid combines readily with bromine in chloroform solution to form, probably, the *dibromide*,



$\left.\begin{array}{l}\text{O·CHPh}\\ \text{CO—CO}\end{array}\right>\text{CH·CHPh·CBr(CHBrPh)·CO·CO}_2\text{H}$, initially, but this loses hydrogen bromide and yields the *dilactone*,



$$\left.\begin{array}{l}\text{O·CHPh}\\ \text{CO—CO}\end{array}\right>\text{CBr·CHPh·CH}\left<\begin{array}{l}\text{CHPh·O}\\ \text{CO——CO}\end{array}\right.;$$

the latter crystallises from alcohol in long, colourless needles which decompose at 196—197°. W. A. D.

Acetals of *p*-Diketohexamethylene. By ROBERT STOLLÉ (*Ber.*, 1901, **34**, 1344—1345).—By heating ethyl succinylsuccinate with ethyl alcohol at 200°, there is obtained together with greenish-yellow crystals melting at 132—133°, the *acetal* of 1 : 4-diketohexamethylene, $C_{14}H_{28}O_4$, which forms colourless plates melting at 89°. Alcohol is eliminated on heating. The *methylacetal* melts at 80—81°. The ethyl derivative is also formed when *p*-diketohexamethylene is heated with ethyl alcohol. K. J. P. O.

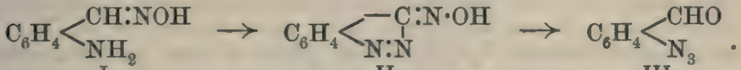
Chemical Action of Light. By GIACOMO L. CIAMICIAN and PAUL G. SILBER (*Atti. Real. Accad. Lincei*, 1901, [v], **10**, i, 228—233. Compare this vol., i, 36).—When *o*-nitrobenzaldehyde is exposed, either in benzene, ether, or acetone solution, or spread out in a thin layer on the walls of a flask to the action of sunlight, it is converted into *o*-nitrosobenzoic acid. In ethyl alcohol solution, *ethyl o-nitrosobenzoate* is obtained in well-developed, colourless crystals melting at 120—121°; when dissolved or melted, the salt gives rise to a green liquid. As *o*-nitrosobenzoic acid does not undergo esterification when exposed in alcoholic solution to the action of light, the reaction between the *o*-nitrobenzaldehyde and alcohol probably results first in the formation of the compound $NO_2·C_6H_4·CH(OH)·OEt$, which is then converted by way of the nitroso-derivative, $NO·C_6H_4·C(OH)_2·OEt$, into ethyl *o*-nitrosobenzoate and water. *Methyl o-nitrosobenzoate*, prepared by the action of sunlight on a methyl alcoholic solution of *o*-nitrobenzaldehyde, crystallises from methyl alcohol in large, rhombic plates, which melt at

152—153° giving an emerald green liquid. An *iso*propyl alcoholic solution of *o*-nitrobenzaldehyde yields *o*-nitrosobenzoic acid and not the *iso*propyl ester.

The action of sunlight on a paraldehyde solution of *o*-nitrobenzaldehyde yields, besides *o*-nitrosobenzoic acid, small quantities of a *compound* having the composition $C_9H_7O_3N$, which crystallises from alcohol in large, colourless prisms melting at 121° and is being further investigated.

When exposed to sunlight in alcoholic solution, neither *m*- nor *p*-nitrobenzaldehyde yields definite products. T. H. P.

o-Aminobenzaldoximes. By EUGEN BAMBERGER and E. DEMUTH (*Ber.*, 1901, **34**, 1309—1339. Compare Abstr., 1899, i, 123).—On diazotising *o*-aminobenzaldoxime (I), condensation of the neighbouring diazo- and aldoxime groups takes place: a condensation which is in no way analogous to the Beckmann transformation of oximes. By the action of alkali hydroxides or hot water, the indiazoneoxime (II), thus produced, is converted into *o*-triazobenzaldehyde (III) (called by the authors, "*o*-azidobenzaldehyde"). The latter on oxidation yields the corresponding acid, which has been synthesised from anthranilic acid.



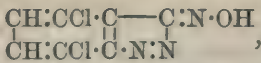
$$C_6H_4{<}\begin{matrix}CH{:}NOH\\NH_2\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}-C{:}N\cdot OH\\ \mid\\ N{:}N\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}CHO\\N_3\end{matrix}.$$

I. II. III.

The *o*-triazobenzaldehydes are colourless, well crystallised substances, very readily volatile in steam and possessing a powerful and characteristic smell.

2-*Triazo*-3:5-*dimethylbenzaldehyde*, $N_3\cdot C_6H_2Me_2\cdot CHO$, prepared by the carefully regulated action of *N* solution of sodium hydroxide on 5:7-dimethylindiazoneoxime (*loc. cit.*), crystallises from petroleum in long, silky, lustrous needles melting at 33·5—34°. It dissolves directly in aqueous sodium hydrogen sulphite and is again precipitated by sodium carbonate. The p-*nitrophenylhydrazone*, crystallises in lustrous orange needles, melting at 153·5—156·5°. Oxidation by means of a 1 per cent. solution of potassium permanganate produces 2-*triazo*-3:5-*dimethylbenzoic acid*, $N_3\cdot C_6H_2Me_2\cdot CO_2H$, which crystallises in needles melting and decomposing at 156°. This acid was also synthesised from 2-aminomesitylenic acid by treating the diazonium perbromide obtained from the latter with concentrated aqueous ammonia. By boiling the triazodimethylbenzaldehyde for 8 hours with excess of *N* sodium hydroxide, it is mainly converted into 2-aminomesitylenic acid.

4:7-*Dichloroindiazoneoxime*,



$$\begin{matrix}CH{:}CCl\cdot C{-\!\!-}C{:}N\cdot OH\\ \mid \qquad\quad \| \qquad \mid\\ CH{:}CCl\cdot C\cdot N{:}N\end{matrix}$$

, prepared by the action of sodium nitrite on 2-amino-3:6-dichlorobenzaldoxime dissolved in acetic acid, crystallises from xylene in needles of a golden-bronze colour, melting and decomposing at 168·5° (corr.). Warm dilute mineral acids decompose this compound, whilst alkali hydroxides slowly dissolve it, forming a yellow solution which rapidly becomes colourless. This change of colour is accompanied by the separation of an oil, which is

2-*triazo*-3 : 6-*dichlorobenzaldehyde*, $C_6H_2Cl_2{\cdot}N_3{\cdot}CHO$. From petroleum, this substance crystallises in needles melting at 86—86·3° (corr.). The p-*nitrophenylhydrazone* forms orange-yellow needles, which decompose at 155°, and when heated at 170°, nitrogen is evolved, and a *compound*, $C_{13}H_8O_2N_4Cl_2$, which is probably a phenotriazine, is obtained. It crystallises in golden-yellow needles melting at 233—234° (corr.). 3 : 6-*Dichloroanthranilic acid*, obtained by the action of alkalis on the triazoaldehyde, forms white needles melting at 154·5—155° (corr.).

Dibromo-o-aminobenzaldoxime, $NH_2{\cdot}C_6H_2Br_2{\cdot}CH{:}NOH$, prepared from the aldehyde (see below), crystallises in needles melting at 189° (corr.). *Dibromoindiazoneoxime* forms golden-yellow needles, which begin to decompose at 178° and explode at 182° (corr.). *Dibromo-o-triazobenzaldehyde*, $N_3{\cdot}C_6H_2Br_2{\cdot}CHO$, forms white, silky needles melting at 75·5—76° (corr.). From it can be obtained *dibromoanthranilic acid*, $NH_2{\cdot}C_6H_2Br_2{\cdot}CO_2H$, which crystallises in needles melting and decomposing at 235—236° (corr.).

Indiazoneoxime (II) is prepared from *o*-aminobenzaldoxime by diazotising in the presence of concentrated hydrochloric acid; it forms golden-yellow needles melting and decomposing at 160—160·5° (corr.). When *o*-aminobenzaldoxime is diazotised in the presence of dilute hydrochloric acid, *o-aldoximophenylazo-o-aldoximoanilide*, $C_{14}H_{13}O_2N_5$, is obtained as a yellow, amorphous solid which decomposes at 73—74°. *o-Triazobenzaldehyde*, $N_3{\cdot}C_6H_4{\cdot}CHO$, prepared from indiazoneoxime, crystallises in transparent, thick plates melting at 37·5°. The *phenylhydrazone* forms pale yellow prisms melting at 101·5—102°; the p-*nitrophenylhydrazone* forms orange red needles melting and decomposing at 191—192°. *o-Triazobenzaldoxime* crystallises in colourless needles melting at 103—103·5°, is soluble in alkalis, and hydrolysed by dilute sulphuric acid. On oxidation, *o*-triazobenzaldehyde yields *o*-triazobenzoic acid, identical with the acid synthesised from anthranilic acid by Griess. Anthranilic acid can be obtained from the triazobenzaldehyde by the prolonged action of boiling aqueous sodium hydroxide.

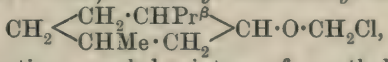
The paper contains a detailed description of the preparation of *o*-aminobenzaldehyde, the p-*nitrophenylhydrazone* of which forms lustrous red leaflets melting at 218°.

Dibromo-o-aminobenzaldehyde, prepared by treating with concentrated ammonia the diazonium perbromide, $C_6H_4N_2Br_3{\cdot}CHO$, obtained from *o*-aminobenzaldehyde, crystallises in elongated light, yellow prisms melting at 137—137·5°. No triazobenzaldehyde is formed in this reaction. K. J. P. O.

Preparation of Aldehydes R·CHMe·CHO by Means of Cyclic Hydrocarbons containing Propenylic Side Chains, such as Anethole, *iso*Safrole, &c. By J. Bougault (*Bull. Soc. Chim.*, 1901, [iii], **25**, 446—448. Compare Abstr., 1900, i, 495, 641).—In the preparation of aldehydes by oxidising anethole, *iso*safrole, &c., with a mixture of iodine and mercuric oxide, as previously described (Abstr., 1900, i, 495), a considerable portion of the aldehyde combines with the alcohol employed. This inconvenience may be avoided by working in moist ethereal, instead of alcoholic, solution. N. L.

Action of Mixed Organomagnesium Compounds on Naphthyl Methyl Ketones. By VICTOR GRIGNARD (*Bull. Soc. Chim.*, 1901, [iii], **25**, 497—499. Compare this vol., i, 250 and 263).—Magnesium methyl iodide reacts with α-naphthyl methyl ketone in ethereal solution to form *α-naphthyldimethylcarbinol*, which crystallises in slender needles melting at 80°. When warmed with acetic anhydride, it yields *βα-naphthylpropylene*, $CH_2\colon CMe\cdot C_{10}H_7$, a colourless liquid boiling at 125° under 8 mm. pressure which has a sp. gr. 1·0208 at 0°, $n_D = 1·61435$ at 9°, and forms a *picrate* crystallising in yellow needles melting at 91°. The action of magnesium methyl iodide on β-naphthyl methyl ketone results in the formation, not of the corresponding carbinol, but of *ββ-naphthylpropylene*, which crystallises in white, nacreous scales melting at 46—47°, boils at 138—140° under 7 mm. pressure, and forms a *picrate* crystallising in orange-yellow needles melting at 88°. *β-Naphthylisoheptylene*, obtained by the action of *iso*amyl magnesium bromide, is a colourless liquid which boils at 175—178° under 10 mm. pressure, has a sp. gr. 0·9808 at 0° and n_D 1·59124 at 9°, and forms a *picrate* crystallising in microscopic, orange needles melting and decomposing at 46—47°. It appears from these results that tertiary β-naphthylcarbinols are unstable and undergo dehydration at the moment of their formation. N. L.

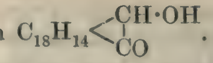
Action of Formaldehyde on Menthol. By EDGAR WEDEKIND (*Ber.*, 1901, **34**, 813—817).—*Menthyl chloromethyl ether*,



$$CH_2<\begin{matrix}CH_2\cdot CHPr^\beta\\ CHMe\cdot CH_2\end{matrix}>CH\cdot O\cdot CH_2Cl,$$

prepared by saturating a cooled mixture of menthol and 40 per cent. aqueous formaldehyde with gaseous hydrogen chloride, boils at 160—162° under 16 mm. pressure and at 230° with partial decomposition under the ordinary pressure, has a sp. gr. 0·9821, and in chloroform has $[\alpha]_D$ −172·57° at 21°; the refractive index is given for the principal lines of the spectrum, n_D being 1·465 at 19°. It is very sensitive to moisture, being rapidly resolved into its components, menthol, formaldehyde, and hydrogen chloride, after the manner of the chlorinated aliphatic ethers, the action in the latter case, however, being far more rapid. On warming with sodium β-naphthoxide in xylene solution, *menthyl β-naphthyl methylene ether*, $C_{10}H_{19}\cdot O\cdot CH_2\cdot O\cdot C_{10}H_7$, melting at 120°, is obtained as a non-crystallisable powder.

Dimenthylmethylal, $CH_2(O\cdot C_{10}H_{19})_2$, prepared by distilling menthyl chloromethyl ether with menthol, crystallises from dilute alcohol in felted needles, melts at 57° (Brochet's "dimentholformal," Abstr., 1899, i, 530, melts at 56·5°), has $[\alpha]_D$ −77·94° at 24°, and is indifferent to boiling acids and alkalis; it has no physiological action, passing through the body unchanged. W. A. D.

Biological Oxidation of Fenchone. By ENRICO RIMINI (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 244—249).—The urine of a dog to which camphor has been administered for some time has been found to contain α- and β-camphoglycuronic acids, and a third acid, to which the name uraminocamphoglycuronic acid has been given; the camphoglycuronic acids can be resolved into glycuronic acid and a compound called camphorol, of the constitution 

$$C_{18}H_{14}<\begin{matrix}CH\cdot OH\\ |\\ CO\end{matrix}$$

. The author has carried out similar experiments with fenchone, which was administered to a dog whose urine was examined to see if products analogous to those obtained in the case of camphor could be found in it. No fenchoneglycuronic acid could be isolated owing to the small quantity of material available, but the presence of such an acid is shown by boiling the liquid with dilute sulphuric acid, by which means a dense, oily liquid was obtained; this gradually deposited acicular crystals of a *compound* which on purification melts at 89° and has the composition $C_{10}H_{16}O_2$. This substance, which is an isomeride of camphorol, is saturated, but is not of an alcoholic or an acid nature. It must be regarded as an oxyfenchone, and is probably analogous with the isomeric compound obtained by Czerny (Abstr., 1900, i, 675) by dissolving fencholenic acid in concentrated sulphuric acid and pouring the liquid on to ice. T. H. P.

Surface Tension and Viscosity of some Essential Oils. By Paul Jeancard and Satie (*Bull. Soc. Chim.*, 1901, [iii], **25**, 519—523).—The surface tension and viscosity of a number of essential oils were determined by Duclaux's method, and the results obtained are given in tabular form. The following general conclusions are arrived at for the different classes of oils. *Alcohol group.*—Oils consisting chiefly of geraniol, free or combined, have a higher surface tension than those having linalool for their principal constituent. The viscosity of esters is much less than that of the corresponding alcohols. Diminution of viscosity generally corresponds with an increase in the saponification number. *Phenol group.*—With oils containing eugenol, the surface tension decreases with the proportion of phenols. The non-phenolic portions of oils containing thymol and carvacrol have a lower viscosity and surface tension than the phenolic portions. *Aldehyde group.*—The surface tension diminishes with the percentage of aldehydes. The viscosity of the aldehydes is generally lower than that of the corresponding alcohols. A few figures are also given for some oils of the ketone and hydrocarbon groups. N. L.

Ethereal Oils. By Schimmel and Co. (*Chem. Centr.*, 1901, i, 1006—1008; from *Geschäftsber.*, April, 1901).—Alpinia oil, prepared by distilling the fresh leaves of *Alpinia malaccensis*, has a sp. gr. 1·02 at 26°, a rotatory power +6·5°, contains methyl cinnamate and about 25 per cent. of compounds which cannot be hydrolysed (compare van Romburgh, this vol., i, 219). From the latter, *d*-pinene was isolated. *d*-Pinene nitrosochloride melts at 108°, and not at 103° as usually stated.

The aqueous distillate of oil of bay contains methyl alcohol, furfuraldehyde, and diacetyl.

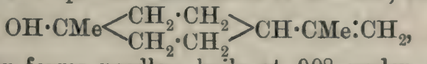
The fractions of higher boiling point and the residue obtained by distilling a French bitter fennel oil contained a substance which separates from alcohol or ethyl acetate in small crystals and melts at 164—165°.

A *ketone* has been isolated from oil of cassia flowers (*Acacia*

Farnesiana) which is probably related to ionone; it has the odour of violets and boils at about 133°. It combines with semicarbazide, forming a *compound* which crystallises in white prisms and melts at 200°, and with *p*-bromophenylhydrazine a compound which melts at 103—107°. The lower fractions of the oil apparently contain benzyl alcohol.

Dowzard's viscosity test (Abstr., 1900, i, 676) is not applicable to oil of lemon as the viscosities of citrene and of oil of lemon are too nearly alike, and tests with different Reischauer viscometers give different results.

Eucalyptus oil from *Eucalyptus aggregata* has a sp. gr. 0·956 and saponification number 112. According to Smith (*J. Proc. Roy. Soc. New South Wales*, 1900, **34**, 72), it contains *d*-pinene and amyl eudesmate, $C_{13}H_{17}\cdot CO_2\cdot C_5H_{11}$. Eudesmic acid, $C_{13}H_{17}\cdot CO_2H$, is an unsaturated acid, crystallises from alcohol in rhombic prisms, and combines with bromine to form a compound which melts at 102—103°. The oil contains neither phellandrene nor cineol. Eucalyptus oil from *Eucalyptus patentinervis* contains citral and probably linalool and geraniol and their esters (compare this vol., i, 282).

Linaloes oil prepared from guayana or cayenne-linaloe wood, has a sp. gr. 0·872—0·875 at 14·5°, $[\alpha]_D$ −15—16° at 13°, and dissolves in 2 parts of 70 per cent. alcohol. It consists almost entirely of *l*-linalool (Theulier, *Rev. gén. Chim. pur. appl.*, 1900, **3**, 262). The physical constants of two German and four Bulgarian rose oils are given in a table in the original paper; the German oils have a lower specific gravity and a smaller rotatory power, but contain more stearoptene. The terpineol which is used in elder perfume, not only contains the inactive terpineol which melts at 35—36°, but also another inactive *terpineol*,  $\mathrm{OH{\cdot}CMe}\left\langle\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\right\rangle\mathrm{CH{\cdot}CMe{:}CH_2}$, of a different odour. The latter forms needles, boils at 90° under 10 and at 209—210° under 752 mm. pressure, has a sp. gr. 0·923 at 15° and n_D 1·4747 at 20°. The *phenylurethane*, $C_{17}H_{23}O_2N$, melts at 85°. The *nitrosochloride* melts at 102—103° and does not readily react with amines. When this terpineol is oxidised first by permanganate and then by chromic acid, it does not yield a ketolactone but an *oxyketone*, $C_9H_{16}O_2$, which boils at 140—145° under 19 mm. pressure and has a sp. gr. 1·023 at 20° and n_D 1·47548 at 20°. The *semicarbazone*, $C_{10}H_{19}O_2N_3$, melts at 195—196°. By the action of bromine and sodium hydroxide solution on the ketone, a *hydroxy-acid*, $C_8H_{14}O_3$, is formed; it melts about 130°, and on warming with concentrated sulphuric acid yields *p*-toluic acid. Wartara oil contains methyl cinnamate.

The paper also contains references to bergamot, atlas cedar, and calamint oils which are not of chemical interest. E. W. W.

Crystalline Component of Calamus Oil. By Hugo von Soden and Wilhelm Rojahn (*Chem. Centr.*, 1901, i, 893—894; from *Pharm. Zeit.*, **46**, 243).—A *compound*, $C_{15}H_{26}O_2$, has been isolated from a Galician calamus oil. It crystallises from methyl alcohol, melts at 165—166°, sublimes at 105—110° without loss of water, is only slightly soluble in the ordinary solvents, and has neither acid nor basic properties. With hydrogen chloride and bromine, it forms additive compounds, and it is not attacked by boiling with acetic anhydride.

E. W. W.

Constituents of Calamus Oil. By HERMANN THOMS and R. BECKSTROEM (*Ber.*, 1901, **34**, 1021—1023).—A fraction of calamus oil, which distilled between 272° and 340° under atmospheric pressure, and had a sp. gr. 1·0254 at 20°, was hydrolysed with alcoholic potash, and the product fractionated under reduced pressure. The portion of highest boiling point, when kept, deposited crystals of a *compound*, $C_{15}H_{26}O_2$, which melted at 166—167·5°. From the alcoholic mother liquor from which this compound separated, asarone was obtained. On extracting the calamus oil with a solution of sodium hydrogen sulphite, an oil is obtained from which crystals of asarylaldehyde slowly separate.

K. J. P. O.

Essence of Geranium from Cannes. By PAUL JEANCARD and SATIE (*Bull. Soc. Chim.*, 1901, [iii], **25**, 516—519. Compare Abstr., 1900, i, 242).—On an average, six specimens per week of essence of geranium from Cannes were examined during the season of 1900, and the minimum, maximum, and mean weekly values of the sp. gr., rotatory power, solubility in 70 per cent. alcohol, surface tension, viscosity, saponification number (hot and cold), free and total alcohols, and ethereal salts are given in the paper in tabular form. The mean results differ but little from those previously obtained (*loc. cit.*). Analyses were also made of the oil after treatment in various ways. Neutralisation diminishes the sp. gr., rotatory power, and surface tension, but increases the solubility. Acetylation increases the sp. gr. and surface tension, but diminishes the viscosity and solubility. Saponification increases the viscosity and solubility. There appears, therefore, to be a connection between the greater solubility and less acidity of the essence from Cannes, as compared with other varieties. The greater part of the free acid is derived from the leaves. N. L.

Essential Oil of Female Rose Wood. By EUGÈNE THEULIER (*Bull. Soc. Chim.*, 1901, [iii], **25**, 468—475).—The wood *Licaria guanensis*, or female rose wood, when distilled with steam yields about 1·5 per cent. of a colourless oil of characteristic odour, having a sp. gr. 0·8727—0·875 at 14·5°, rotatory power −15·2° to −15·5° at 13°, and saponification number 1·385; it is soluble in two volumes of 70 per cent. alcohol, and distils between 192° and 210°. The oil consists almost entirely of *l*-linalool, with less than 1 per cent. of esters which could not be identified; methylheptenone is absent. N. L.

Algerian Oil of Rue. By HUGO VON SODEN and KARL HENLE (*Chem. Centr.*, 1901, i, 1006; from *Pharm. Zeit.*, **46**, 277).—An Algerian oil of rue has been found to possess properties differing from those of the ordinary oil. Its odour not only resembled that of rue, but was also somewhat similar to that of fatty ketones. It had a sp. gr. 0·842 at 15°, a rotatory power −5° (100 mm. tube), a saponification number 64, and consisted mainly of *methyl heptyl ketone*, together with a small quantity of methyl nonyl ketone, and esters of unknown alcohols. The methyl heptyl ketone, $COMe\cdot C_7H_{15}$, is probably the normal ketone; it is a colourless oil, boils at 193—194° under 740 mm. pressure, has a sp. gr. 0·821 at 20°, and solidifies at $-15°$. The *semicarbazone*, $C_7H_{15}\cdot CMe\colon CH_3ON_3$, crystallises in lustrous leaflets and melts at 118—119°. E. W. W.

Essential Oil of Vetiver. By EUGÈNE THEULIER (*Bull. Soc. Chim.*, 1901, [iii], **25**, 454—465).—Essential oil of vetiver, iwarancusa, or cuscus, obtained by steam distillation from the roots of *Andropogon Muricatus*, is a dark, greenish-brown, viscous liquid, soluble in 1·5 vols. of 80 per cent. alcohol. Two specimens distilled (1) at Grasse, and (2) at Reunion gave the following results:

	(1)	(2)
Sp. gr. at 20°	1·0091	0·986
Rotatory power at 20°	+35·10°	+28°
Acid number	32·48	6·16
Saponification number	11·92	12·12

The acidity of the oil appears to be due to an acid corresponding with a sesquiterpenic alcohol. From the behaviour of the oils on fractional distillation, it is concluded that the two varieties contain the same constituents, but in different proportions. N. L.

The Resin of Pinus Sylvestris. By ALEXANDER TSCHIRCH and B. NIEDERSTADT (*Arch. Pharm.*, 1901, **239**, 167—181).—The sample examined was collected in Finland it had acid number about 161, saponification number equal to this, and iodine number 65·7. By distilling it, traces of succinic acid were obtained, and a *bitter substance* was extracted with hot water.

From an ethereal solution of the resin, ammonium carbonate solution extracts nothing. A mixture of acids is extracted by 1 per cent. aqueous sodium carbonate. From a solution of these in a mixture of methyl and ethyl alcohols, *silveolic acid*, $C_{14}H_{20}O_2$, crystallises; this melts at 138°, and has acid (and saponification) number 262 (corresponding with monobasicity), and iodine number 57·7 (corresponding with the formation of a monoiodo-compound); its crystalline *potassium* and *barium* salts were analysed. The other acids are amorphous, but form lead salts that are respectively insoluble and soluble in alcohol, and thus can be separated. The former, *a-silvinolic acid*, $C_{15}H_{26}O_2$, melts at 85—90°, has acid (and saponification) number 232 (corresponding with monobasicity), and iodine number 53·3 (corresponding with the formation of a monoiodo-compound). The second acid *β-silvinolic acid*, $C_{14}H_{24}O_2$, melts at 89—95°, and has acid (and saponification) number 247 (corresponding with monobasicity), and iodine number 56·5 (corresponding with the formation of a monoiodo-compound). From the residual ethereal solution after the removal of these acids, aqueous potassium hydroxide extracts nothing further.

The ether was distilled off and the residue distilled with steam, when an *essential oil* passed over, boiling at 155—163°, and with a sp. gr. 0·840.

There remained indifferent *silvoresen*, melting at 58—60°.

In 100 parts of the drug there are contained:—silveolic acid, 1·5;

silvinolic acids, α and β, 58—60; essential oil 15; silvoresen 20—21; bitter substance, succinic acid, and impurities 1—2. C. F. B.

New Zealand Kauri Copal from Dammara Australis. By ALEXANDER TSCHIRCH and B. NIEDERSTADT (*Arch. Pharm.*, 1901, **239**, 145—167).—The sample examined was a recent fossil specimen of Kauri copal from New Zealand; it melted at 110—125°, had acid number about 107, saponification number only slightly higher, and iodine number 45·7. When it is distilled, only 2 per cent. of carbon remains in the retort; acetic and formic acids can be detected in the distillate, but not succinic acid. A *bitter substance* can be extracted with water.

From an ethereal solution of the copal, 1 per cent. aqueous ammonium carbonate extracts *kauric acid*, $C_{10}H_{16}O_2$. This melts at 192°, has a specific rotation 51·7° in 2 per cent. alcoholic solution, acid (and saponification) number 332·5 (corresponding with monobasicity) and iodine number 75·8 (corresponding with the formation of a monoiodo-compound); the anhydrous *potassium* and *lead* salts were analysed. Oudeman's podocarpic acid, $C_{17}H_{22}O_3$ (*Onderz Naturk. Verh. K. Akad. Wetensch. Amsterdam*, 1873, **14**), resembles kauric acid in some respects, but has acid (and saponification) number 205, and iodine number 46·1.

From the ethereal solution, 1 per cent. aqueous sodium carbonate now extracts amorphous isomeric α- and *β-kaurolic acids*, $C_{12}H_{20}O_2$, the lead salts of which are respectively insoluble and soluble in alcohol. The acids melt at 81—83° and 85—87° respectively; both have acid (and saponification) number 279 (corresponding with monobasicity), and iodine number 64·4 (corresponding with the formation of a monoiodo-compound).

From the ethereal solution now remaining, 1 per cent. aqueous potassium hydroxide extracts two amorphous acids, the lead salts of which are respectively insoluble and soluble in alcohol. The former of these, *kaurinolic acid*, $C_{17}H_{34}O_2$, melts at 128—130°, has acid (and saponification) number 203 (corresponding with monobasicity), and iodine number 46·9 (corresponding with the formation of a monoiodo-compound). The second, *kauronolic acid*, $C_{12}H_{24}O_2$, melts at 86—89°, has acid (and saponification) number 272 (corresponding with monobasicity) and iodine number 63·15 (corresponding with the formation of a monoiodo-derivative).

When the ethereal solution is freed finally from ether and the residue distilled with steam, an *essential oil* comes over, boiling at 150—160°, mostly at 156—160°, and with a sp. gr. 0·835 at 15°.

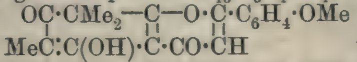
The residue not volatile with steam, *kauroresen*, is an indifferent substance melting at 63—65°; it was not pure, however.

In 100 parts of the drug there are contained:—kauric acid, 1·5; kaurolic acids, 48—50; kaurinolic and kauronolic acids, 20—22; essential oil, 12·5; kauroresen, 12·2; bitter substance, 0·5—1.

C. F. B.

Apiin and Apigenin. By A. CONTI and GIUSEPPE TESTONI (*Gazzetta*, 1901, **31**, i, 73—77).—On hydrolysing crude apiin by means of dilute sulphuric acid, a yellowish powder is obtained which, when acetylated, yields (1) a *triacetyl* derivative which separates from alcohol in slender white needles melting at 215°; this is derived from the parent substance of the composition $OMe\cdot C_{15}H_6O_2(OH)_3$, which is probably a flavone derivative; (2) diacetylapigenin, and (3) triacetylapigenin.

The action of methyl iodide and alcoholic potassium hydroxide yields a *methyl* derivative of apigenin having the composition $C_{15}H_6O_4Me_4\cdot OMe$, and the probable constitution



$$\begin{array}{l} OC\cdot CMe_2-C-O\cdot C\cdot C_6H_4\cdot OMe \\ \quad | \qquad\qquad\quad \| \qquad\; \| \\ MeC{:}C(OH)\cdot C\cdot CO\cdot CH \end{array}$$

; it separates from alcohol in yellow, acicular crystals melting at 185°, and on oxidation with nitric acid yields anisic acid. T. H. P.

Natal Aloes. By Alexander Tschirch and J. Klaveness (*Arch. Pharm.*, 1901, **239**, 231—240. Compare Léger, *Bull. Soc. Chim.*, 1900, [iii], **23**, 790).—The powdered aloes were macerated with strong alcohol, and the undissolved aloin crystallised from 70 per cent. alcohol; the yield was 15—16 per cent. No substance corresponding with Léger's homonataloin could be detected. Nataloin, $OMe\cdot C_{15}H_{10}O(OH)_5$, is yellow and crystallises in quadratic tablets or plates; when crystallised from alcohol only, it has no definite melting point, but if crystallised first from acetic acid and then from alcohol, it melts at 202—204°; it is anhydrous, although it loses weight when heated in a current of hydrogen gas. It forms a yellowish, amorphous *penta-acetyl* derivative melting at 125—126°, together with a small quantity of a crystalline acetyl derivative, which melts at about 240° and contains C 60·6, H 6·15 per cent.; this was regarded by Tilden (*Chem. News*, 1872, **25**, 229) as hexa-acetylnataloin, but it is probably derived from a condensation product. Nataloin also forms a *pentabenzoyl* derivative melting at 168°; it yields oxalic and picric acids when oxidised with nitric acid; when chromic mixture is used, small quantities of fatty acids are formed. When boiled with alcoholic hydrochloric acid, it appears to yield a little emodin.

The resin was precipitated from the alcoholic extract by adding water, and purified by repetition of this treatment (compare Abstr., 1898, i, 599); the mother liquors yielded amorphous *nataloin-red* when neutralised with ammonia and evaporated. The resin was hydrolysed by prolonged boiling with 2 per cent. aqueous potassium carbonate; from the aqueous solution so obtained, sulphuric acid precipitates the resinotannol, whilst ether extracts *p*-coumaric acid, $OH\cdot C_6H_4\cdot CH{:}CH\cdot CO_2H$, from the liquid remaining. The resin of Natal aloes is thus *nataloresinotannol* p-*coumarate*. *Nataloresinotannol*, $C_{22}H_{18}O_4(OH)_4$, is a brown powder; it gives a brownish-black coloration with ferric chloride, forms a *tetrabenzoyl* derivative as a light brown powder, and yields oxalic and picric acids when oxidised with nitric acid, and fatty acids and phloroglucinol when fused with potash. C. F. B.

Aniline-Black. By Ernst Börnstein (*Ber.*, 1901, **34**, 1284—1291).—When aniline-black is oxidised with potassium dichromate, quinone is produced; when it is fused with potassium hydroxide, *p*-diphenylphenylenediamine is obtained, together with a small quantity of a violet *substance*, which has a coppery lustre and is soluble in alcohol, chloroform or acetone.

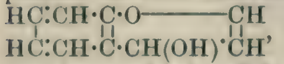
Aniline-black may be obtained in good yield, either by Müller's method (Abstr., 1871, 1098) or by the oxidation of aniline with ammonium persulphate. By extracting the product of the former method with hot toluene, bye-products were obtained which were separated by alcohol into soluble and insoluble portions. The soluble portion yielded yellow plates melting at 223°, red needles melting at 185°, and a third substance which forms dark red crystals and melts at 177°; all these compounds contain chlorine, but the quantities obtained were too small for further examination. The insoluble portion was found to consist of a mixture of two compounds which were separated by a method depending on a marked difference in their densities. The lighter *substance*, $C_{24}H_{18}O_2N_3Cl$, crystallises in yellowish, brown needles which have a violet lustre, melts at 337°, and sublimes at a higher temperature without decomposition; when it is warmed with a mixture of sulphuric acid and alcohol, aniline is produced together with a brown *substance*, which crystallises in small, four-sided tablets and melts at 277°; if it is distilled with zinc dust, it yields aniline and a *substance* which crystallises in microscopic red needles. The heavier *substance*, $C_{30}H_{21}O_2N_4Cl_3$, crystallises in dark brown leaflets and melts at 286°; when heated with alcoholic sulphuric acid, aniline is produced together with a yellow, crystalline *substance*. E. G.

2-Acetylfurfuran from Wood-Tar and its Synthesis. By LOUIS BOUVEAULT (*Ber.*, 1901, **34**, 1072—1073. Compare Abstr., 1899, i, 120).—The synthesis described by the author has been repeated by Sandelin (Abstr., 1900, i, 305).

2-Acetylfurfuran is best obtained from wood-tar by treatment with 30 per cent. sulphuric acid. The portion dissolved by acid of this strength is treated with sodium hydrogen sulphite, and the insoluble part distilled, when the 2-acetylfurfuran passes over between 65° and 70°. The *benzoyl* derivative of the *oxime* forms colourless crystals and melts at 97—98°. The *semicarbazone* crystallises in yellow needles melting at 148°. A. H.

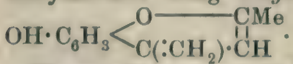
Nomenclature of Coumarone Derivatives. By RICHARD STOERMER (*Ber.*, 1901, **34**, 1148—1150. Compare Abstr., 1900, i, 650).—Polemical. A reply to Simonis (*Ber.*, 1901, **34**, 781). J. J. S.

Derivatives of 1 : 4-Benzopyranol, the Mother Substance of a New Class of Colouring Matters. By CARL BÜLOW and HERMANN WAGNER (*Ber.*, 1901, **34**, 1189—1210).—Acetylacetone and other 1 : 3-diketones and aldehydoketones readily condense with phenols to form derivatives of 1 : 4-benzopyranol (1 : 4-chromanol),



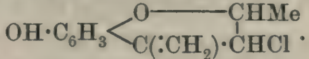
$$\begin{array}{l} HC{:}CH\cdot C\cdot O\text{———}CH \\ HC{:}CH\cdot C\cdot CH(OH)\cdot CH \end{array}$$

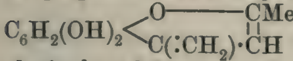
, the compound derived from resorcinol and acetylacetone being *7-hydroxyanhydro-2 : 4-dimethyl-1 : 4-benzopyranol*,



$$OH\cdot C_6H_3 < \begin{array}{l} O\text{———}CMe \\ C({:}CH_2)\cdot CH \end{array}.$$

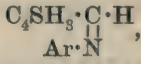
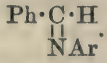
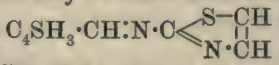
These substances, which are closely related to the derivatives of flavone, have basic properties and their hydrochlorides act as dyes. The constitution follows from the mode of preparation and from the nature of the products obtained by the action of 10 per cent. aqueous potash.

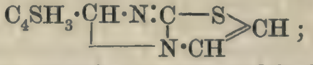
7-Hydroxyanhydro-2:4-dimethyl-1:4-benzopyranol is obtained by the condensation of resorcinol with acetylacetone in acetic acid solution in presence of hydrogen chloride, and forms an amorphous, orange-coloured mass. The *hydrochloride*, $C_{11}H_{10}O_2,HCl$, crystallises with $1H_2O$ in straw-yellow coloured prisms and is decomposed by water. It becomes dark coloured at 160° and black at 200°. This salt probably has the constitution  $OH\cdot C_6H_3<\begin{matrix}O\text{———}CHMe\\ C(:CH_2)\cdot CHCl\end{matrix}$. The solution in sulphuric acid shows an intense green fluorescence.

The colour base is decomposed by boiling aqueous potash, yielding resacetophenone and acetone, and the constitution which has been assigned to it is thus confirmed. The *picrate*, $C_{11}H_{10}O_2,C_6H_3O_7N_3$, crystallises in greenish-yellow, rhombic tablets. Acetic anhydride in presence of sodium acetate and acetic acid yields an *acetyl* derivative, $OAc\cdot C_6H_3\cdot C_5H_6O$, which is a faintly yellow powder, and softens and becomes resinous at 150—155°. A methyl derivative could not be prepared. 5 : 7-*Dihydroxyanhydro*-2 : 4-*dimethyl*-1 : 4-*benzopyranol*,  $C_6H_2(OH)_2<\begin{matrix}O\text{———}CMe\\ C(:CH_2)\cdot CH\end{matrix}$, is prepared from acetylacetone and phloroglucinol, and forms a yellow, microcrystalline powder containing $1H_2O$, which is lost at 115°. Aqueous potash converts it into acetone, phloroglucinol, and acetic acid, the latter two substances being probably products of the secondary decomposition of 2 : 4 : 6-trihydroxyacetophenone. The *hydrochloride* forms a lemon-yellow, crystalline powder which blackens at 250°. The solution in sulphuric acid shows no fluorescence. The *picrate* crystallises in small, yellow prisms and the *acetyl* derivative is a yellowish-white, amorphous powder and softens at 145—155°.

7 : 8-*Dihydroxyanhydro*-2 : 4-*dimethyl*-1 : 4-*benzopyranol* is obtained from acetylacetone and pyrogallol and is a violet-red, amorphous powder which decomposes above 150°; when treated with aqueous potash, it yields gallacetophenone and acetone. The *hydrochloride* forms dark orange crystals containing $1H_2O$, decomposes above 200°, and forms a non-fluorescent solution in sulphuric acid. The *picrate* crystallises in fascicular groups of slender needles, and the *acetyl* derivative is a yellowish-white, amorphous powder. A. H.

Phenanthroxazine. By FRANCIS JAPP and WILLIAM B. DAVIDSON (*Ber.*, 1901, **34**, 806).—Phenanthroxazine (Bamberger and Grob, this vol., i, 280) is identical with the compound $C_{28}H_{17}ON$, obtained by the authors (Trans., 1895, **67**, 47). C. F. B.

Anils of Thiophenaldehyde. By ARTHUR HANTZSCH and RUDOLF WITZ (*Ber.*, 1901, **34**, 841—847).—Thiophenaldehyde and aniline yield on condensation a yellow *oil* which was not analysed. *Thiophenidene*-p-*toluidine*, $C_4SH_3\cdot CH:N\cdot C_6H_4Me$, obtained by warming the aldehyde with the base, crystallises from alcohol in yellow prisms and melts at 36°. *Thiophenidene*-p-*bromoaniline* forms bright yellow leaflets and melts at 90°. The foregoing compounds exist only in one form, which has probably the configuration  $\begin{matrix}C_4SH_3\cdot C\cdot H\\ Ar\cdot N\end{matrix}$, since the hydrochlorides are stable in contact with water and in this respect resemble the stable hydrochlorides of the *syn*-aldoximes, and differ from the unstable hydrochlorides of the *anti*-aldoximes and of the benzaldehydeanils, which have the configuration  $\begin{matrix}Ph\cdot C\cdot H\\ NAr\end{matrix}$. *Thiophenideneaminothiazole* exists in two forms which may be either stereoisomerides or tautomerides having the structure  $C_4SH_3\cdot CH{:}N\cdot C{<}\begin{matrix}S-CH\\ N\cdot CH\end{matrix}$ and



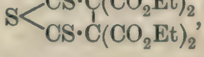
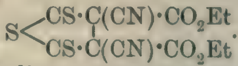
$$C_4SH_3\cdot CH\cdot N{:}C\begin{matrix}-S\\ N\cdot CH\end{matrix}{>}CH\,;$$

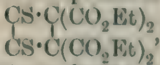
the *a-form*, obtained on warming thiophenaldehyde with aminothiazole (1 mol.), crystallises from alcohol in bright yellow leaflets, melts at 109°, and is converted at this temperature, when heated in nitrogen, into the *β-form* melting at 47—48°, which again changes, either on recrystallisation from alcohol or after 7 or 8 days at the ordinary temperature, into the a-form. *Thiophenidenebisaminothiazole*,

$$C_4SH_3\cdot CH(C_3H_3N_2S)_2,$$

the product of the action of thiophenaldehyde with 2 mols. of aminothiazole, melts at 117° with decomposition into its components; when dissolved in *p*-toluidine, thiophenidene-*p*-toluidine is formed along with 2 mols. of aminothiazole, as shown by determinations of the molecular weight by the cryoscopic and ebullioscopic methods. Benzylidene-bisaminothiazole (this vol., i, 378) is decomposed similarly by *p*-toluidine.

W. A. D.

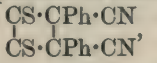
Action of Halogens and Carbon Disulphide on Sodium-Methylene Compounds. By G. WENZEL (*Ber.*, 1901, 34, 1043—1050).—The compounds obtained by the author (Abstr., 1900, i, 536) by the action of bromine and carbon disulphide on ethyl sodiomalonate and ethyl sodiocyanoacetate have the composition $C_{16}H_{20}O_8S_3$ and $C_{12}H_{10}O_4N_2S_3$ respectively, and not $C_{16}H_{22}O_8S_3$ and $C_{12}H_{12}O_4N_2S_3$, as at first supposed. The former compound is *ethyl dithiotetrahydrothiophentetracarboxylate*,  $S{<}\begin{matrix}CS\cdot C(CO_2Et)_2\\ CS\cdot C(CO_2Et)_2\end{matrix}$, whilst the latter is the *diethyl* ester of the corresponding *dinitrile*,  $S{<}\begin{matrix}CS\cdot C(CN)\cdot CO_2Et\\ CS\cdot C(CN)\cdot CO_2Et\end{matrix}$.

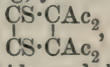
When bromine or iodine is added to ethyl sodiocyanoacetate suspended in cold carbon disulphide, Errera and Perciabosco's ethyl tricyanotrimethylenetricarboxylate (this vol., i, 18) is produced; if, however, the carbon disulphide is heated to boiling before the addition of the halogen, the diethyl ester of the dinitrile of dithiotetrahydrothiophentetracarboxylic acid is obtained. If the carbon disulphide is heated in the preparation of the tetraethyl ester, the yield of this compound is increased, and *ethyl dithiotetramethylenetetracarboxylate*,  $\begin{matrix}CS\cdot C(CO_2Et)_2\\ CS\cdot C(CO_2Et)_2\end{matrix}$, is simultaneously formed, which crystallises in colourless, feathery needles, and melts at 179—180°; it is identical with the ethyl thiocarbonylmalonate obtained by Bergreen (Abstr., 1888, 445) by the action of thiocarbonyl chloride on ethyl sodiomalonate. *Dithiotetramethylenetetracarboxylic acid* crystallises in white needles, decomposes at 310°, and cannot be recrystallised without change; it is also produced by the hydrolysis of ethyl dithiotetrahydrothiophentetracarboxylate; its *potassium*, *sodium*, *ammonium*, *barium*, and *calcium* salts were prepared.

Ethyl dithiobutanetetracarboxylate, $CH(CO_2Et)_2\cdot CS\cdot CS\cdot CH(CO_2Et)_2$ obtained by reduction of ethyl dithiotetramethylenetetracarboxylate with zinc dust and acetic acid, crystallises in long, colourless needles, melts at 103°, and is soluble in acetone or dilute alcoholic alkali.

When the diethyl ester of the dinitrile of dithiotetrahydrothiophentetracarboxylic acid is heated with bromine and water, the *dibromo*-additive product, $C_4SBr_2S_2(CN)_2(CO_2Et)_2$, is obtained as a yellow oil; it crystallises from alcohol in yellow, prismatic needles, melts at 95—96°, and is not affected when heated with silver at 200—250°.

If an alcoholic solution of ethyl dithiotetramethylenetetracarboxylate is heated with phenylhydrazine, hydrogen sulphide is produced, and on cooling, the *tetraphenylhydrazine* salt separates in lustrous leaflets.

Dithiodiphenyltetramethylenedinitrile,  $\begin{array}{l}CS\cdot CPh\cdot CN\\ \vert\quad\ \vert\\ CS\cdot CPh\cdot CN\end{array}$, obtained by the action of carbon disulphide and bromine on sodiobenzyl cyanide, crystallises from dilute acetone in long, yellow needles and melts at 174°.

Dithiotetra-acetyltetramethylene,  $\begin{array}{l}CS\cdot CAc_2\\ \vert\quad\ \vert\\ CS\cdot CAc_2\end{array}$, produced in small quantity by the action of carbon disulphide and bromine on sodium acetylacetone, crystallises from glacial acetic acid in golden-yellow prisms, and melts at 230°; it may be obtained in better yield from sodium acetylacetone and thiocarbonyl chloride. E. G.

Oxidation of Arginine. I. By ELOPHE BÉNECH and FR. KUTSCHER (*Zeit. physiol. Chem.*, 1901, **32**, 278—280).—On oxidation with barium permanganate, arginine yields guanidine, which is best isolated in the form of its picrate. The second product of oxidation is undoubtedly α-amino-*n*-valeric acid, and arginine is thus guanidine-α-aminovaleric acid. J. J. S.

Tautocinchonine. By FRIEDRICH LANGER (*Monatsh.*, 1901, **22**, 151—156).—*allo*Cinchonine is the chief product formed on removing, by means of alcoholic silver nitrate, hydrogen bromide from trihydrobromocinchonine prepared either from the commercial or carefully purified cinchonine dihydrobromide. The commercial product yielded also a base with a higher melting point (261°), which is apparently identical with the tautocinchonine obtained by von Lowenhaupt (Abstr., 1899, i, 176). This base is, however, a mixture from which some 40 per cent. of cinchotine can be isolated. With alcoholic potash, trihydrobromocinchonine similarly yields chiefly *allo*cinchonine, together with some δ-cinchonine and α-*iso*cinchonine. K. J. P. O.

Bases Analogous to Nichine from Cinchonine. By FRIEDRICH LANGER (*Monatsh.*, 1901, **22**, 157—170).—δ-Cinchonine hydrochloride prepared from trihydrobromocinchonine, by von Lowenhaupt's method (Abstr., 1899, i, 176) is shown to have the formula $C_{18}H_{22}ON_2,HCl,1\frac{1}{2}H_2O$. From this fact and from the composition of other derivatives, the base must be represented by the formula $C_{18}H_{22}ON_2$, and not $C_{19}H_{22}ON_2$ as hitherto supposed. The base melts at 141·5—142° and has $[\alpha]_D$ +139·45° at 20°. δ-Cinchonine thus bears the same relation to cinchonine as nichine does to quinine.

The acid *δ-cinchonine dihydriodide*, $C_{18}H_{22}ON_2,2HI$, forms plates melting at 232°. By the action of concentrated hydriodic acid the latter forms an *additive product*, $C_{18}H_{22}ON_2,3HI$, which crystallises in needles melting at 243—244°. The base, hydriodo-δ-cinchonine is converted into δ-cinchonine by the action of alcoholic silver nitrate.

Nitroso-δ-cinchonine, $C_{18}H_{21}ON_2\cdot NO$, prepared from δ-cinchonine hydrochloride by the action of sodium nitrite, forms an amorphous powder which gives Liebermann's reaction.

Hydriodocinchonine, when treated with alcoholic silver nitrate, yields a base, which appears to be identical with δ-cinchonine.

Hydrochlorocinchonine, under the action of alcoholic potash, is converted into a *base*, $C_{19}H_{22}ON_2$, and α-*iso*cinchonine. The former melts at 170·5—171°, and has $[\alpha]_D$ −7·0° at 20°; the *hydrochloride* crystallises in leaves. K. J. P. O.

Transformation or Cinchonine by means of Sulphuric Acid. By Zdenko H. Skraup (*Monatsh.*, 1901, **22**, 171—190. Compare Abstr., 1899, i, 961).—Sulphuric acid is far less effective in producing the transformation of cinchonine into α- and β-*iso*cinchonine than hydrogen chloride, bromide, or iodide. The change, however, proceeds with measurable velocity when concentrations from 19·5 to 30·5 *N* sulphuric acid are used.

The changes, which occur may be represented as follows: cinchonine $\longrightarrow$ α-*iso*cinchonine $\rightleftarrows$ β-*iso*cinchonine $\rightleftarrows$ *allo*cinchonine. Of these the two latter are to a certain extent reversible. Concomitantly with the transformation of any given alkaloid, sulphonation of that alkaloid or the formation of a sulphuric acid additive product is effected. The change of cinchonine into α-*iso*cinchonine takes place with so much greater velocity than the change of the latter into β-*iso*cinchonine, that practically the whole of the cinchonine disappears before any β-*iso*cinchonine is formed. In the action of sulphuric acid on cinchonine, the proportion of the alkaloid converted into α-*iso*cinchonine is approximately three times that sulphonated. An account is given in the paper of the quantitative experiments from which these results are deduced, and of the methods of estimating cinchonine, and α- and β-*iso*cinchonine in mixtures containing the three alkaloids.

The sulphonic acid derivatives were not obtained in a pure state, but a *cupric* salt, $C_{19}H_{22}ON_2\cdot SO_4Cu$ was isolated. K. J. P. O.

***allo*Cinchonine.** By Ottokar Josef Hlavnička (*Monatsh.*, 1901, **22**, 191—205).—*allo*Cinchonine, prepared by the action of silver nitrate on hydriodocinchonine, yields a *dihydriodide* melting at 236—239° and crystallising in pale yellow prisms, and a normal *sulphate*, $C_{19}H_{22}ON_2,H_2SO_4,3H_2O$, crystallising in large prisms.

By the action of concentrated hydriodic acid on *allo*cinchonine, the dihydriodide and an *additive* compound, $C_{19}H_{25}ON_2I_3$, melting at 227° are formed. By the action of alcoholic potash on trihydriodo-*allo*cinchonine, *a*-*iso*cinchonine and *allo*cinchonine are obtained. With phenylhydrazine, this alkaloid does not react.

Phenylcarbimide gives a *derivative*, $C_{19}H_{21}ON_2\cdot CO\cdot NHPh$, which forms colourless prisms melting at 191·5—192°, and is decomposed by hydrochloric acid with the production of aniline. In this reaction with phenylcarbimide, *allo*cinchonine resembles cinchonine, and is distinguished from *a*- and *β*-*iso*cinchonine.

On heating the normal sulphate previously mentioned at 140°, a tarry mass is produced from which a base can be obtained. The *oxalate* of this base, $(C_{19}H_{22}ON_2)_2,C_2H_2O_4,13H_2O$, forms silky needles melting at 170°. The base, prepared from the oxalate, reacts with phenylhydrazine, yielding a *phenylhydrazone*, $C_{19}H_{22}ON_2\colon N_2HPh$, a red, brittle solid melting at about 94—96°. By heating with 63 per cent. sulphuric acid, *allo*cinchonine is chiefly converted into *β*-*iso*cinchonine, together with a small amount of a sulphonic acid.

K. J. P. O.

Bases in Mandragora Roots. By HERMANN THOMS and M. WENTZEL (*Ber.*, 1901, **34**, 1023—1026. Compare Abstr., 1898, i, 708).—Besides the alkaloid hyoscyamine, the authors have now succeeded in isolating another alkaloid, scopolamine, from mandragora roots. The roots in a fine state of division are extracted with alcoholic tartaric acid; the acid extract, after neutralisation with sodium hydrogen carbonate, is thoroughly extracted with ether, by which means the whole of the scopolamine, which is not strongly basic, together with a small amount of the more strongly basic hyoscyamine, pass into the ether. By fractional crystallisation of the aurichlorides, pure scopolamine aurichloride is obtained, melting at 204°. The hydrobromide obtained by a similar process is shown to be identical in optical activity, &c., with that prepared by Schmidt (Abstr., 1892, 1255).

K. J. P. O.

Morphidine. By EDUARD VONGERICHTEN (*Ber.*, 1901, **34**, 1162—1164. Compare this vol., i, 767).—The substance, obtained in very small quantity, together with phenanthrene on distilling morphine with zinc dust, and previously described as morphidine (*Ber.*, 1901, **34**, 767), is in reality a mixture of two bases. The two bases appear to be practically identical in properties with the exception that the methiodide of one of them is readily decomposed by sodium hydroxide, whilst the other is not. To the *platinichlorides*, the formulæ $(C_{17}H_{16}N)_2PtCl_6$ and $(C_{17}H_{14}N)_2PtCl_6$, are ascribed respectively.

J. J. S.

Alkaloids of Peganum Harmala. By OTTO FISCHER (*Chem. Centr.*, 1901, i, 957—959; from *Festschr. zum* 80 *Geburtstag des Prinzregenten Luitpold*, Erlangen, 1901. Compare Abstr., 1885, 821; 1889, 730, and 1898, i, 164).—Harmalol has been isolated from the seeds of *Peganum harmala*, and is identical with the product obtained by the action of concentrated hydrochloric acid on harmaline; the green fluorescence of its aqueous solution is almost completely destroyed by acids or alkalis. Harmine melts at 257—259°. Harminic acid is an ortho-dicarboxylic acid, but on titration behaves like a monobasic acid, one carboxyl group being combined as in a salt. Apoharmine is decomposed by potassium permanganate, forming ammonia and oxalic acid; its nitro-derivative has both acid and basic properties (compare the nitroiminazoles of Bamberger and Berlé). The *aurichloride* crystallises in orange-yellow needles concentrically arranged. Harmol cannot be directly reduced by the action of hydriodic acid or of zinc dust, but the oxygen may be eliminated indirectly by means of the amino-derivative.

Aminoharman, $C_{12}H_{11}N_3$, prepared by the action of ammonio-zinc chloride and ammonium chloride on harmol at 250°, crystallises from water in flat needles or leaflets, has a silvery lustre, sinters at 292°, melts at 298°, sublimes with partial decomposition, and is easily soluble in alcohol. The solutions of the salts show a blue fluorescence. The *hydrochloride* crystallises in colourless prisms, and is slightly soluble in water; the *nitrate* and *sulphate* were also prepared. *Harman*, $C_{12}H_{10}N_2$, obtained by diazotising the amino-derivative, resembles harmine, and separates in leaflets or flat needles; it crystallises from benzene in small, stout crystals, melts at 230°, sublimes with partial decomposition, forming a sublimate which crystallises in needles, and is readily soluble in ethyl or methyl alcohol. Its solution in concentrated sulphuric acid has a faint blue fluorescence, whilst the solutions of its salts show a strong blue fluorescence. The *platinichloride*, $(C_{12}H_{10}N_2)_2,H_2PtCl_6,\frac{1}{2}H_2O$, crystallises in pale yellow needles and is slightly soluble in water; the *aurichloride* separating in matted, orange needles and the *mercurichloride* was also prepared.

Harmaline crystallises from alcohol or benzene in large, colourless crystals which, in thicker layers, appear yellow. Its solution in concentrated sulphuric acid is intensely yellow but not fluorescent, whilst the alcoholic solutions of the yellow salts have a green fluorescence. By the action of hydrochloric acid on a boiling solution of acetylharmaline in alcohol, the solution becomes brown, green, and finally dirty blue, and from the product ammonia precipitates a strong *base*, $C_{15}H_{18}O_3N_2$, in almost colourless needles or leaflets; it separates from water in yellow crystals, melts at 164—165°, is easily soluble in hot water, and forms yellow solutions in acids. The *platinichloride*, $(C_{15}H_{18}O_3N_2)_2,H_2PtCl_6$, crystallises in lustrous, brown needles, and decomposes at 210°. The *aurichloride* is difficult to obtain in a crystalline form. The *mercurichloride* was also prepared. The base is only reconverted into harmaline by prolonged boiling with alcoholic potash, and by the action of hydrochloric acid at 150—160° it forms harmalol. When harmaline is boiled with nitric acid of sp. gr. 1·48, nitroanisic acid $[OMe : NO_2 : CO_2H = 1 : 2 : 4]$ is formed together with harminic acid. The former acid is derived from methoxynitrophthalic acid by elimination of carbon dioxide. The harmaline alkaloids must therefore contain a complex, $OMe{\cdot}C_6H_3(C{-})C$, in which $OMe : C : C = 1 : 3 : 4$ or $1 : 4 : 5$.

The physiological effect of these alkaloids is to reduce the temperature.

A summary of all the known derivatives of this group is given in the original paper.

E. W. W.

Acid Chlorides of the Pyridine Series. By HANS MEYER (*Monatsh.*, 1901, **22**, 109—117).—The pyridinecarboxylic acids are converted into the chlorides by gently heating the acid with thionyl chloride in a sealed tube.

Picolinic chloride, $C_5NH_4\cdot COCl$, forms small, colourless needles melting at 220° which sublime without decomposing. With water, it yields the hydrochloride of picolinic acid, and with alcohol the ethyl ester.

Nicotinic chloride, $C_5NH_4\cdot COCl$, a white powder, melts and decomposes at 245°; it combines with hydrogen chloride to form the hydrochloride.

iso*Nicotinic chloride*, $C_5NH_4\cdot COCl$, forms white needles melting and decomposing at 270°, and melting at 240—245° in a closed capillary tube.

Cinchonic acid reacts very readily with thionyl chloride, forming the *hydrochloride* of the chloride, $C_9NH_6\cdot COCl,HCl$, which crystallises in faintly yellow needles melting at 170°. *Cinchonic chloride* is obtained as yellow needles by allowing the hydrochloride to stand over sodium hydroxide. It melts at 109° and distils at 210°. *Methyl cinchonate*, prepared from the acid chloride by the action of methyl alcohol, melts at 24°.

With thionyl chloride, quinolinic and cinchomeronic acids yield only the anhydrides. K. J. P. O.

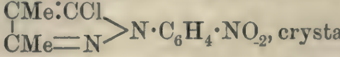
Constitutional Formula of Fischer's Base. By KARL BRUNNER (*Gazzetta*, 1901, **31**, i, 181—183).—A reply to Plancher, who claims priority in putting forward the constitutional formula of Fischer's base (1 : 3 : 3-trimethyl-2-methyleneindoline). T. H. P.

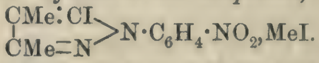
Chloro-*m*-phenylenediamine. By PAUL COHN (*Monatsh.*, 1901, **22**, 118—222. Compare Abstr., 1900, i, 458).—By the reduction of chlorodinitrobenzene (1 : 3 : 5) with stannous chloride, 5-chloro-*m*-phenylenediamine is prepared; it forms prisms melting at 105—106°, which belong to the rhombic system [$a : b : c = 1 : 0{\cdot}7115 : 0{\cdot}4709$]. The *hydrochloride, sulphate*, and *platinichloride* all crystallise well; the first named readily darkens in the air. The *diacetyl* derivative forms light brown needles, which do not melt at 300°; the *dibenzoyl* derivative crystallises in needles melting at 254—255°.

With benzenediazonium salts, the base gives an azo-dye, and by Sandmeyer's reaction it is easily converted into 1 : 3 : 5-trichlorobenzene. K. J. P. O.

Some 5-Halogen-phenylalkylpyrazoles. By AUGUST MICHAELIS, U. VOSS and MAX GREISS (*Ber.*, 1901, **34**, 1300—1308).—5-Chloro-1-phenyl-3 : 4-dimethylpyrazole (Michaelis and Röhmer, Abstr., 1899, i, 233) is a colourless liquid of remarkable odour, which boils at 281° and forms thick, colourless crystals melting at 26°; its *hydrochloride* sublimes on heating and is decomposed by water; the *platinichloride* crystallises with $2H_2O$, and melts at 176°. The *methiodide*,

$$C_{11}H_{11}N_2Cl,MeI,$$

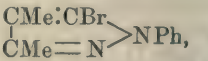
crystallises in white leaflets and melts at 235°. The corresponding *methochloride* forms hygroscopic crystals; its *platinichloride* $(C_{11}H_{11}N_2Cl,MeCl)_2,PtCl_4$, crystallises in yellow needles. When the methiodide or methochloride is treated with alcoholic potassium hydroxide, it is converted into 1-phenyl-2 : 3 : 4-trimethylpyrazolone. On reduction of chlorophenyldimethylpyrazole with hydriodic acid, phenyldimethylpyrazole is obtained, whilst by the action of sodium on an alcoholic solution, phenyldimethylpyrazoline is produced. The p-*nitro*-derivative,  $\left.\begin{array}{l}\mathrm{CMe{:}CCl}\\ \mathrm{CMe{=}N}\end{array}\right>\mathrm{N{\cdot}C_6H_4{\cdot}NO_2}$, crystallises in white needles and melts at 140° ; when heated at 110° with excess of methyl iodide, it yields yellowish-red crystals of the *compound*,



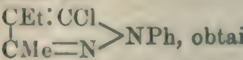
$$\left.\begin{array}{l}\mathrm{CMe{:}Cl}\\ \mathrm{CMe{=}N}\end{array}\right>\mathrm{N{\cdot}C_6H_4{\cdot}NO_2,MeI}.$$

The corresponding *amino*-derivative, $C_3N_2Me_2Cl{\cdot}C_6H_4{\cdot}NH_2$, crystallises in white leaflets and melts at 75—78°. *Chlorodinitrophenyldimethylpyrazole*, $C_3N_2Me_2Cl{\cdot}C_6H_3(NO_2)_2$, forms lustrous crystals and melts at 121° ; the corresponding diamino-derivative could not be obtained.

5-*Chloro*-1-*phenyl*-3-*methylpyrazole*-4-*carboxylic acid*, obtained by the oxidation of chlorophenyldimethylpyrazole with chromic acid, crystallises in plates, melts at 228—229°, and dissolves easily in ether or glacial acetic acid ; it does not combine with methyl iodide. When this acid is heated in a closed tube at 230—240°, carbon dioxide and 5-chloro-1-phenyl-3-methylpyrazole are produced. The acid *chloride* melts at 85°, and by the action of water is readily converted into the acid. The *amide* melts at 183°, and dissolves readily in alcohol and sparingly in ether.

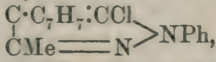
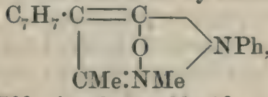
5-*Bromo*-1-*phenyl*-3 : 4-*dimethylpyrazole*,  $\left.\begin{array}{l}\mathrm{CMe{:}CBr}\\ \mathrm{CMe{=}N}\end{array}\right>\mathrm{NPh}$, obtained by heating the corresponding chloropyrazole with ethyl bromide at 210° in a sealed tube, forms transparent crystals, melts at 51°, and boils at 210—220° under 100 mm. and at 295° under atmospheric pressure. The *methobromide*, $C_{11}H_{11}N_2Br,MeBr$, crystallises in white leaflets and melts and decomposes at 230°.

When chlorophenyldimethylpyrazole is heated with ethyl iodide, the *ethiodide* of the corresponding iodopyrazole, $C_{11}H_{11}N_2I,EtI$, is produced, which crystallises in white, pearly leaflets and melts and decomposes at 222—223°. The *ethochloride*, $C_{11}H_{11}N_2I,EtCl,4H_2O$, obtained by shaking a hot aqueous solution of the ethiodide with silver chloride, crystallises in small, white prisms and melts at 85° ; the anhydrous substance melts at 190°. When the ethochloride is distilled under 25—30 mm. pressure, it yields ethyl chloride and 5-*iodo*-1-*phenyl*-3 : 4-*dimethylpyrazole*, which forms pale yellow crystals, melts at 78°, and is soluble in ether or alcohol. The ethiodide of 5-iodo-1-phenyl-3-methylpyrazole (Michaelis and Pasternack, Abstr., 1899, ii, 942) can be similarly converted into the ethochloride, and by distilling this in a vacuum, the pyrazole itself is obtained as an almost colourless oil.

5-*Chloro*-1-*phenyl*-3-*methyl*-4-*ethylpyrazole*,  $\left.\begin{array}{l}\mathrm{CEt{:}CCl}\\ \mathrm{CMe{=}N}\end{array}\right>\mathrm{NPh}$, obtained by the action of phosphorus oxychloride on phenylmethylethylpyrazolone, forms white crystals, melts at 40°, and boils at 175° under 50° mm. and at 285° under atmospheric pressure ; its *platinichloride* forms large, red crystals containing $1H_2O$, and melts at 173°. The *methiodide* melts at 176°, the *methobromide* at 197°, and the *methochloride* at 162°; when these compounds are treated with alcoholic potassium hydroxide, 4-ethylantipyrine is produced. The *nitro*-derivative,

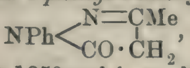
$$C_3N_2MeEtCl\cdot C_6H_4\cdot NO_2,$$

crystallises in white needles, melts at 71°, and on reduction is converted into the *amino*-derivative melting at 107°; the *dinitro*-derivative melts at 138°. When the pyrazole is oxidised with chromic acid, it is converted into 5-chloro-1-phenyl-3-methylpyrazole-4-carboxylic acid. The *pyrazoline*, $\begin{matrix} CHEt\cdot CH_2 \\ | \\ CMe{=\!=}N \end{matrix}\!\!>NPh$, obtained by the action of sodium on an alcoholic solution of the pyrazole, is a pale yellow liquid which boils at 294°; its *nitro*-derivative crystallises in yellow needles and melts at 121°.

1-Phenyl-4-benzyl-3-methylpyrazolone, first obtained by Walker (Abstr., 1894, i, 476) by the action of benzyl chloride on phenylmethylpyrazolone, may also be prepared by the condensation of ethyl benzylacetoacetate with phenylhydrazine; when heated with phosphorus oxychloride, it is converted into *5-chloro-1-phenyl-4-benzyl-3-methylpyrazole*,  $\begin{matrix} C\cdot C_7H_7{:}CCl \\ | \\ CMe{=\!=}N \end{matrix}\!\!>NPh$, which crystallises in colourless prisms and melts at 50°. The *methiodide* of the last-mentioned compound melts at 167°, and is converted by alcoholic potassium hydroxide into *benzylantipyrine*,  which crystallises in needles and melts at 70°; its *hydrochloride* melts at 167°. The *nitro*-derivative of the chloropyrazole melts at 128°, and on reduction yields the *amino*-derivative which crystallises in white leaflets and melts at 100°. E. G.

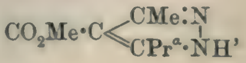
Action of Phenylhydrazine and Hydrazine on the Two Isomeric Methyl Butyrylacetoacetates. By A. Bongert (*Compt. rend.*, 1901, **132**, 973—975. Compare this vol., i, 311).—Methylbutyrylacetoacete (C-ester) and phenylhydrazine interact, giving rise to acetylphenylhydrazine, *phenylpropylpyrazolone*, $C_{12}H_{14}ON_2$, and a *bispyrazolone*, $(C_{12}H_{13}ON_2)_2$; the former of these new compounds melts at 108° and boils at about 200° under 10 mm. pressure; the latter, which is insoluble in neutral solvents, crystallises in needles from glacial acetic acid and melts at 346°; it readily dissolves in dilute acids and alkaline solutions, and develops with ferric chloride an intense blue coloration.

With phenylhydrazine, the O-ester (methyl butyryloxymethacrylate) yields methyl alcohol, *butyrylphenylhydrazine*, crystallising in silky needles melting at 102° and 1-*phenyl-3-methylpyrazolone*,



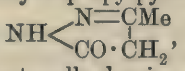
$$NPh<\begin{matrix} N{=\!=}CMe \\ \quad\ | \\ CO\cdot CH_2 \end{matrix},$$

a compound which melts at 125° and is readily soluble in ether, alcohol, or dilute acid or alkaline solutions.

Methyl 3-methyl-5-propylpyrazole-4-carboxylate,  $CO_2Me\cdot C<\begin{matrix} CMe{:}N \\ \quad | \\ CPr^{a}\cdot NH \end{matrix}$,

produced by mixing in alcoholic solutions equal mols. of hydrazine and methyl butyrylacetoacetate (C-ester), is a viscid oil boiling at 179° under 10 mm. pressure; it yields a crystalline derivative with hydrochloric acid which is readily decomposed by hot water or cold dilute alkaline solutions.

The *acid* obtained by hydrolysing the preceding ester with 20 per cent. potassium hydroxide separates from ether or alcohol in white crystals and melts at 226°; when heated at higher temperatures, it evolves carbon dioxide and yields an oil having a pungent odour which is in all probability 3-methyl-5-propylpyrazole.

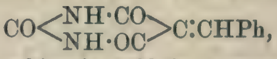
3-*Methyl-5-pyrazolone*,  $\mathrm{NH}{<}\begin{matrix}\mathrm{N{=}CMe}\\ \quad\;\; | \\ \mathrm{CO\cdot CH_2}\end{matrix}$, melting at 215—216°, is formed together with butyrylhydrazine and methyl alcohol by the action of hydrazine on the O-ester.

Benzylidenebutyrylhydrazone, $C_3H_7\cdot CO\cdot NH\cdot N{:}CHPh$, produced by mixing together benzaldehyde and butyrylhydrazine in the presence of a solution of an alkali hydroxide, crystallises in silky needles and melts at 96°.

The *butyrylhydrazone* of acetone melting at 83° results from the action of butyrylhydrazine on acetone; it is very soluble in the ordinary organic solvents with the exception of light petroleum.

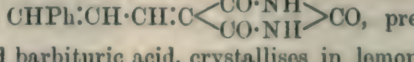
G. T. M.

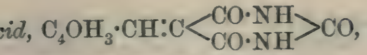
Condensation of Barbituric Acid with Aldehydes. By MAX CONRAD and H. REINBACH (*Ber.*, 1901, **34**, 1339—1344).—Barbituric acid readily condenses with aldehydes in the absence of any condensing agent.

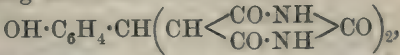
Benzylidenebarbituric acid,  $\mathrm{CO}{<}\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot OC}\end{matrix}{>}\mathrm{C{:}CHPh}$, prepared by heating equal quantities of barbituric acid in aqueous solution and benzaldehyde for 1 or 2 hours on the water-bath, forms colourless prisms from boiling acetic acid which melt at 256°. On treatment with cold aqueous sodium hydroxide or ammonia, it decomposes with the formation of benzaldehyde. Benzylbarbituric acid is obtained on reduction with zinc dust and acetic acid.

o-*Nitrobenzylidenebarbituric acid*, $C_{11}H_7O_5N_3$, forms crystals which become coloured at 240° and melt and decompose at 250—252°. With aqueous ammonia, it yields a yellow *additive product*, $C_{11}H_{10}O_5N_4$.

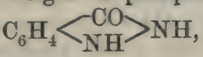
o-Aminobenzaldehyde and barbituric acid give a *compound*, $C_{11}H_7O_2N_3$, which is formed by the elimination of water from the *o*-aminobenzylidenebarbituric acid first produced. It decomposes above 280° without melting and can be sublimed. It exhibits both acid and basic properties, and forms a *hydrochloride*, $C_{11}H_7O_2N_3,HCl$, and a *sodium* salt, $C_{11}H_6O_2N_3Na,2H_2O$, as a yellow precipitate. On heating the latter at 200°, ammonia is evolved; when the residue is treated with hydrochloric acid, carbon dioxide is given off, and carbostyril-3-carboxylic acid is obtained.

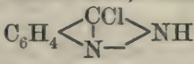
Cinnamylidenebarbituric acid,  $\mathrm{CHPh{:}CH\cdot CH{:}C}{<}\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CO\cdot NH}\end{matrix}{>}\mathrm{CO}$, prepared from cinnamaldehyde and barbituric acid, crystallises in lemon-yellow prisms melting and decomposing at 226—228°.

Furfurylidenebarbituric acid,  $C_4OH_3\cdot CH{:}C<^{CO\cdot NH}_{CO\cdot NH}>CO$, forms an insoluble yellow powder decomposing above 280°.

Salicylidene-bis-barbituric acid,  $OH\cdot C_6H_4\cdot CH\left(CH<^{CO\cdot NH}_{CO\cdot NH}>CO\right)_2$, obtained from salicylaldehyde and barbituric acid, is a white, crystalline powder which darkens at 225° and melts and decomposes at 260°.

K. J. P. O.

Indazole. By Emil Fischer and Otto Seuffert (*Ber.*, 1901, 34, 795—798).—When *o*-hydrazinobenzoic acid, $NH_2\cdot NH\cdot C_6H_4\cdot CO_2H$, or more conveniently its hydrochloride, is boiled under atmospheric pressure with 6—7 times its weight of phosphorus oxychloride, it is converted into the anhydride,  $C_6H_4<^{CO}_{NH}>NH$, this being the best way of preparing the last substance. The excess of oxychloride is distilled off under diminished pressure, and the anhydride dissolved in dilute aqueous sodium hydroxide and precipitated with acetic acid.

When *o*-hydrazinobenzoic acid hydrochloride (or, less well, the anhydride) is heated for 4 hours with seven times its weight of phosphorus oxychloride at 120° in a sealed tube, instead of in an open vessel, the product is chloroindazole,  $C_6H_4<^{CCl}_{\overset{|}{N}-}>NH$ (Bamberger, Abstr., 1899, i, 546), of which the *acetyl* derivative melts at 67°, the *nitroso*-derivative at 89—90°. Chloroindazole can be reduced to indazole with zinc powder and strong hydrochloric acid; this must be liberated with ammonia, not with sodium hydroxide, as it forms a compound with zinc hydroxide. It is thus possible to prepare indazole starting from anthranilic acid, which is now a cheap substance. Chloroindazole also forms *methylchloroindazole*, $C_8H_7N_2Cl$, a very feebly basic substance boiling at 268·5° under a pressure of 754 mm., when it is boiled with methyl iodide and methyl alcoholic potassium hydroxide; this yields methylaniline when heated with soda-lime. Further, chloroindazole, when heated at 100° with benzaldehyde in the presence of zinc chloride, forms *benzylidenediindazole*, $CHPh(C_7H_5N_2)_2$, which melts at 140—141°, and is insoluble in dilute acids, as well as in water.

C. F. B.

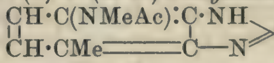
Formation of Aromatic Quaternary Ammonium Compounds. By Johannes Pinnow (*Ber.*, 1901, 34, 1129—1138. Compare Abstr., 1899, i, 588).—According to Fischer and Windaus (Abstr., 1900, i, 224), a rule similar to Victor Meyer's esterification rule holds for the formation of quaternary ammonium iodides from the tertiary aromatic base and methyl iodide, no quaternary iodide being formed if both the ortho-positions to the dimethylamino-group are replaced. The formation or non-formation of a quaternary ammonium compound is hence suggested as a means of determining the position of the amino-groups in aromatic bases. The authors find, however, that such a rule does not hold in all cases. Thus, neither from *m*-nitrodimethyl-*p*-toluidine nor from nitroacetylaminodimethyltoluidine [$NMe_2 : NHAc : Me : NO_2 = 4 : 3 : 1 : 6$] is an ammonium iodide formed with methyl iodide, whilst

4-acetylamino-1 : 2 : 5-trimethylbenziminazole (see this vol., i, 139) takes up methyl iodide almost quantitatively.

Pure *m*-nitrodimethyltoluidine and methyl iodide do not combine, but if traces of dinitrotolylmethylnitrosoamine are present, a small quantity of a methiodide is formed.

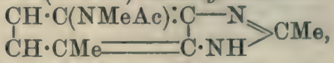
o-*Nitro*-m-*acetylaminodimethyl*-p-*toluidine*, $C_{11}H_{15}O_3N_3$, prepared by nitrating the substituted base below 0°, crystallises from a mixture of alcohol and ether in bright yellow, rhombic plates which melt at 142·5—143° (uncorr.), and dissolve readily in chloroform, acetone, or ethyl acetate, less so in alcohol or benzene, and only slightly in ether, light petroleum, or water. This compound only gives a small quantity of methiodide when heated with methyl iodide.

When γ-diacetyldiaminomethyltoluidine is treated with glacial acetic acid, two products are obtained : (1) 4-acetylamino-1 : 2 : 5-trimethylbenziminazole, which on hydrolysis yields 4-amino-1 : 2 : 5-trimethylbenziminazole ; the latter yields a *tartrate*, $C_{10}H_{13}N_3,C_4H_6O_6$, crystallising from water in needles arranged in nodular aggregates, and a *hydrochloride* (+ H_2O) separating in shining, oblique prisms and rhomboidal plates. (2) 7- (or 4-) *Acetylmethylamino*-2 : 4- (or 2 : 7-) *dimethylbenziminazole*,



$$\begin{array}{l} CH\cdot C(NMeAc){:}C\cdot NH \\ \| \qquad\qquad\qquad | \\ CH\cdot CMe=\!=\!=\!=C-N \end{array}\!\!>\!CMe$$

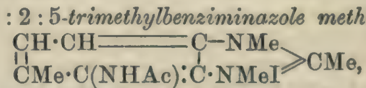
or



$$\begin{array}{l} CH\cdot C(NMeAc){:}C-N \\ | \qquad\qquad\qquad | \\ CH\cdot CMe=\!=\!=\!=C\cdot NH \end{array}\!\!>\!CMe,$$

which crystallises from water, with $3H_2O$, in slender needles and melts in its water of crystallisation at 64—65°, after beginning to sinter at 61° ; when dried by gradual heating to 97° in a vacuum, it melts at 198—198·5° (uncorr.) ; it is soluble in alcohol, acetone, or ethyl acetate.

4-*Acetylamino*-1 : 2 : 5-*trimethylbenziminazole methiodide*,



$$\begin{array}{l} CH\cdot CH=\!=\!=\!=\!=C-NMe \\ \| \qquad\qquad\qquad | \\ CMe\cdot C(NHAc){:}C\cdot NMeI \end{array}\!\!>\!CMe,$$

prepared from its components either alone or in presence of methyl alcohol, or from γ-diacetyldiaminomethyltoluidine, methyl iodide, and methyl alcohol, separates from a mixture of alcohol and acetone in crystals melting at 232°. When treated with lead acetate and alcohol, the iodine is replaced by an acetyl group, and on oxidising the methylacetyl compound thus obtained by means of permanganate, it yields

4-*Acetylamino*-1 : 3-*dimethylbenziminazolone*-5-*carboxylic acid*,

$$C_{12}H_{13}O_4N_3,$$

which crystallises from a mixture of alcohol and acetic acid in almost white prisms, remains unmelted at 270°, and is readily soluble in acetic acid.

The following mixtures were experimented with to ascertain if quaternary ammonium compounds could be obtained from them : Dimethyl-*p*-toluidine, methyl alcohol, and hydrobromic acid ; *p*-toluidine hydrobromide and methyl alcohol ; *p*-toluidine hydrochloride and methyl alcohol ; *o*-nitrodimethyl-*p*-toluidine, methyl alcohol, and hydrogen bromide ; *p*-toluidine hydrochloride, methyl alcohol, and benzene ; dimethyltoluidine, ethyl bromide, and benzene ; *o*-nitrodimethyltoluidine, ethyl bromide, and benzene ; *o*-acetylaminodimethyl-*p*-toluidine, ethyl bromide, and benzene ; *m*-acetylaminodimethyl-*p*-toluidine, methyl iodide, and benzene ; *m*-acetylaminodimethyl-*p*-toluidine, ethyl bromide, and benzene. The results are arranged in tabular form. The following quaternary salts were isolated.

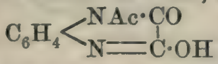
o-*Nitro*-p-*tolyltrimethylammonium bromide*, $C_{10}H_{14}O_2N_2,HBr$, crystallises from alcohol in clusters of bright yellow, oblique prisms which melt at 182° (uncorr.) and dissolve readily in water.

o-*Acetylamino*-p-*tolyldimethylethylammonium bromide*, $C_{13}H_{20}ON_2,HBr$, melts at 187·5° (uncorr.), but could not be obtained crystalline as it is too soluble in water, alcohol, or aqueous acetone and not sufficiently so in other solvents.

m-*Acetylamino*-p-*tolyltrimethylammonium iodide*, $C_{12}H_{18}ON_2,HI$, crystallises from a mixture of alcohol and ether in rhombic needles having a brilliant lustre and melting at 193·5° (uncorr.); it is soluble in alcohol or water but insoluble in ether.

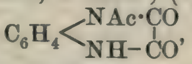
The presence of water hinders the formation of the quaternary ammonium salts. T. H. P.

Quinoxaline Group. I. By C. MANUELLI and M. GALLONI (*Gazzetta*, 1901, **31**, i, 18—26).—The action of anhydrous oxalic acid on diacetyl-*o*-phenylenediamine gives rise to three products: (1) methylbenziminazole; (2) *monoacetyl*-o-*phenylenediamine*, $C_8H_9ON_2$, which melts at 145° and is soluble in water, alcohol, or ether; (3) *monoacetyldioxyquinoxaline*,



$C_6H_4 \langle {}^{NAc \cdot CO}_{N \!=\!=\! C \cdot OH}$

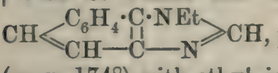
or



$C_6H_4 \langle {}^{NAc \cdot CO}_{NH - CO}$,

which crystallises from water in small, white prisms melting at 184°; it dissolves in alcohol, chloroform, acetic acid, or aqueous alkali hydroxides, and to a slight extent in benzene or ether. The *hydrochloride*, $C_{10}H_8O_3N_2,HCl$, is very soluble in water or alcohol and melts at 176·5°; the *platinichloride*, $(C_{10}H_8O_3N_2)_2,H_2PtCl_6$, separates from ether in shining, yellow prisms melting at 215°; the *mercurichloride*, $(C_{10}H_8O_3N_2)_2,HgCl_2$, crystallises from dilute hydrochloric acid in long, white prisms melting at 191—192°; the *diethiodide*, $C_{10}H_8O_3N_2,2EtI$, separates from alcohol in long, slender, dark red, unstable needles melting at 115°. No oxime or phenylhydrazone could be prepared. T. H. P.

Iminazoles of the Benzene and Naphthalene Series. By OTTO FISCHER (*Ber.*, 1901, **34**, 930—940. Compare Abstr., 1899, i, 641).—[With O. FEZER and LUDWIG REINDL.]—1-*Ethyl-α-naphthiminazole*,

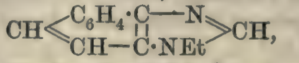


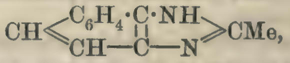
$CH \langle {}^{C_6H_4 \cdot C \cdot NEt}_{CH - C - N} \rangle CH$,

prepared by heating, at 110°, naphthiminazole (m. p. 174°) with ethyl iodide and absolute alcohol, crystallises from ether in colourless prisms and melts at 129—130°; its *hydriodide* is not completely decomposed by cold aqueous sodium hydroxide solution, the base being, however, set free by digesting the salt with alcoholic potassium hydroxide. The *platinichloride* crystallises in pale yellow needles, and the *mercurichloride* in colourless needles, the latter melting at 162°.

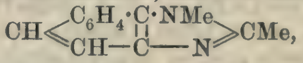
1-*Methyl-α-naphthiminazole* crystallises from ether or alcohol in colourless needles melting at 88°. The *platinichloride* and *aurichloride* separate from alcohol in yellow needles.

1-*Acetyl-α-naphthiminazole*, produced by treating naphthiminazole with acetic chloride in pyridine solution, crystallises from benzene in white needles and melts at 153°; the corresponding *benzoyl* derivative, obtained by the Schotten-Baumann reaction, melts at 120°.

3-*Ethyl-β-naphthiminazole*,  $\mathrm{CH}{<}\begin{array}{l}\mathrm{C_6H_4{\cdot}C{-}N}\\ \mathrm{CH{-}C{\cdot}NEt}\end{array}{>}\mathrm{CH}$, obtained by heating β-ethyl-1 : 2-naphthylenediamine with formic acid, is an oil distillable under reduced pressure; the *hydrochloride* crystallises from alcohol in colourless needles and melts at 226°; the *mercurichloride* forms slightly soluble, white needles and melts at 182°.

2-*Methyl-α-naphthiminazole*,  $\mathrm{CH}{<}\begin{array}{l}\mathrm{C_6H_4{\cdot}C{\cdot}NH}\\ \mathrm{CH{-}C{-}N}\end{array}{>}\mathrm{CMe}$, prepared by heating at 140° for 12 hours a mixture of 1 : 2-naphthylenediamine hydrochloride, sodium acetate, and glacial acetic acid, is obtained in the form of its *hydrochloride* by extracting the product of reaction with water and allowing the solution to crystallise; the free base is slightly soluble in water or ether and crystallises from methyl alcohol in lustrous prisms melting at 168—169°. The *mercurichloride* crystallises in white prisms, and the *aurichloride*, $C_{12}H_{11}N_2Cl_4Au$, in orange needles; the *platinichloride*, when separating from hot aqueous solutions, contains $3H_2O$, this water being eliminated at 110—120°.

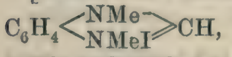
1 : 2-*Dimethyl-α-naphthiminazole hydriodide*, prepared by heating the preceding base with methyl iodide at 100°, crystallises from hot water in aggregates of colourless needles; the free *base*,

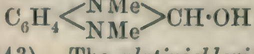


$$\mathrm{CH}{<}\begin{array}{l}\mathrm{C_6H_4{\cdot}C{\cdot}NMe}\\ \mathrm{CH{-}C{-}N}\end{array}{>}\mathrm{CMe},$$

crystallises from dilute alcohol in colourless needles and melts at 143—144°; the *platini-* and *auri-chlorides* crystallise in yellow needles.

2-*Phenyl-α-naphthiminazole*, produced on heating at 160° a mixture of 1 : 2-naphthylenediamine hydrochloride, sodium benzoate, and benzoic acid, is isolated in the form of its *benzoate*, this salt separating from alcoholic solutions in white, nodular crystals; the base separates from dilute alcohol in colourless crystals melting at 217°. The *nitrate* and *sulphate* crystallise in white needles, the *aurichloride* in reddish-brown prisms melting at 207°, and the *platinichloride* in pale yellow needles with $2H_2O$.

[With E. Fussenegger.]—1 : 3-*Dimethylbenziminazole iodide*,  $\mathrm{C_6H_4}{<}\begin{array}{l}\mathrm{NMe{-}}\\ \mathrm{NMeI}\end{array}{>}\mathrm{CH}$, obtained by heating benziminazole with methyl iodide and methyl alcohol at 140—150°, melts at 144°.

1 : 3-*Dimethylbenziminazolone*, prepared either by treating the preceding compound with sodium hydroxide or by the action of formic acid on *s*-dimethyl-*o*-phenylenediamine, crystallises in white needles and melts at 74—75°, its *hydrochloride* melts at 247°; the second method of preparation indicates that the base has the constitution of a carbinol,  $\mathrm{C_6H_4}{<}\begin{array}{l}\mathrm{NMe}\\ \mathrm{NMe}\end{array}{>}\mathrm{CH{\cdot}OH}$ (compare Pinnow and Sämann, Abstr., 1899, i, 943). The *platinichloride* and *aurichloride* do not contain oxygen; the former crystallises in red prisms, the latter in yellow needles.

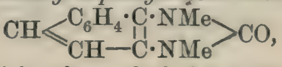
s-*Dimethyl*-o-*phenylenediamine*, $C_6H_4(NHMe)_2$, produced by hydrolysing the preceding base or its salts with aqueous sodium hydroxide solution, is distillable in steam, boils at 245—255°, and melts at

34—35°; it forms crystallisable salts, the *hydrochloride* melting at 180°. A solution of the hydrochloride develops, with ferric chloride a red coloration, and a hydrochloride, crystallising in green leaflets, is subsequently produced; this product, which readily dissolves in water, is less soluble in alcohol and yields a yellow base.

s-Dimethyl-*o*-phenylenediamine, when condensed with acetic anhydride, yields 1 : 2 : 3-trimethylbenziminazolone (compare Pinnow and Sämann, *loc. cit.*), this synthesis confirming the constitution ascribed to the substance.

Dimethylphenylenecarbamide, $C_6H_4{<}\begin{array}{c}NMe\\NMe\end{array}{>}CO$, is readily obtained from 1 : 3-dimethylbenziminazolone either by oxidation with potassium permanganate or by dry distillation; in the latter process, 1-methylbenziminazole is simultaneously produced.

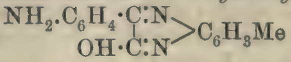
1 : 3-*Dimethylnaphthiminazolone*, $CH{<}\begin{array}{l}C_6H_4{\cdot}C{\cdot}NMe\\ \qquad\ \ \|\\ CH{-}C{\cdot}NMe\end{array}{>}CH{\cdot}OH$, produced by the action of methyl iodide and methyl alcohol on 1-methyl-*a*-naphthiminazole or naphthiminazole, crystallises in colourless prisms and melts at 123°; when boiled with aqueous sodium hydroxide solution, oxidised with potassium permanganate, or subjected to dry distillation, it yields *dimethylnaphthylenecarbamide*,



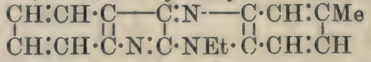
$$CH{<}\begin{array}{l}C_6H_4{\cdot}C{\cdot}NMe\\ \qquad\ \ \|\\ CH{-}C{\cdot}NMe\end{array}{>}CO,$$

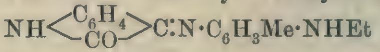
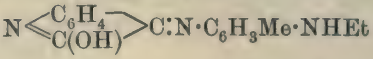
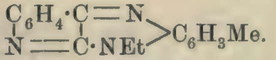
this compound crystallising from alcohol in white prisms and melting at 171°. G. T. M.

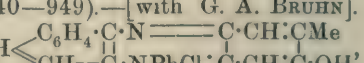
Isatin and its Derivatives. VI. By LEO MARCHLEWSKI and J. SOSNOWSKI (*Ber.*, 1901, **34**, 1108—1112).—The compound formed by the hydrolysis of the product of condensing acetylisatin with *o*-phenylenediamine is not *o*-aminophenimesatin (Abstr., 1896, i, 235) but 2-*hydroxy*-3-o-*aminophenylquinoxaline*, $\begin{array}{r}NH_2{\cdot}C_6H_4{\cdot}C{:}N\\ |\ \ \ \\ OH{\cdot}C{:}N\end{array}{>}C_6H_4$; when hydrochloric acid and sodium nitrite are added to its boiling alcoholic solution, it yields *cumarophenazine*, $\begin{array}{l}C_6H_4{\cdot}C{:}N\\ |\qquad\ \ |\\ O{-}{-}C{:}N\end{array}{>}C_6H_4$, which crystallises from dilute alcohol in lustrous, scaly aggregates of slender needles or in long, yellow needles, melts at 168° (uncorr.), and sublimes unchanged at higher temperatures. Although a neutral substance, it dissolves in boiling alkalis to form 2-*hydroxy*-3-o-*hydroxyphenylquinoxaline*, $\begin{array}{r}OH{\cdot}C_6H_4{\cdot}C{:}N\\ |\ \ \ \\ OH{\cdot}C{:}N\end{array}{>}C_6H_4$, which crystallises from alcohol in dark yellow needles, melts at 296° (uncorr.) (289° when slowly heated), and readily yields a *monosulphonic acid* crystallising in slender, golden needles; the *sodium* salt of the latter crystallises from a mixture of water and alcohol in long, yellowish-brown needles containing water of crystallisation, and the *barium* salt forms bright yellow needles and is sparingly soluble in water.

Methylcumarophenazine, $\begin{array}{l}C_6H_4{\cdot}C{:}N\\ |\qquad\ \ |\\ O{-}{-}C{:}N\end{array}{>}C_6H_3Me$, obtained by the action of hydrochloric acid and sodium nitrite on 2-*hydroxy*-3-o-*aminophenyl*-6-(or 7)-*methylquinoxaline*,  $\begin{array}{l}NH_2.C_6H_4\cdot C\colon N\\ OH\cdot C\colon N\end{array}>C_6H_3Me$ (to be described later), separates from alcohol in white crystals, melts at 133—134° (uncorr.), and closely resembles its homologue; thus, when boiled with alkalis, it yields 2-*hydroxy*-3-o-*hydroxyphenyl*-6-(or 7)-*methylquinoxaline*, which melts at 161° and is easily sulphonated.

Both cumarophenazine and methylcumarophenazine show a blue fluorescence in alcoholic solution. W. A. D.

Isatin. VII. By Leo Marchlewski and L. G. Radcliffe (*Ber.*, 1901, **34**, 1113—1115).—Isatin interacts with ethyl-*o*-tolylenediamine, $NHEt\cdot C_6H_3Me\cdot NH_2$ [$Me:NH_2:NHEt = 1:3:4$], in glacial acetic acid, not as a diketone, but as a hydroxyketone, to form 5-*ethyl*-2-*methyl*-ψ-*indophenazine*,  $\begin{array}{l}CH\colon CH\cdot C{-\!\!-}C\colon N{-\!\!-}C\cdot CH\colon CMe\\ CH\colon CH\cdot C\cdot N\colon C\cdot NEt\cdot C\cdot CH\colon CH\end{array}$; this crystallises from dilute alcohol in lustrous red needles, melts at 213°, and yields yellow *salts* which are hydrolysed by hot water.

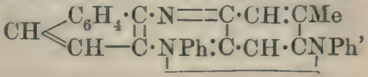
It is probable that isatin does not react initially as a hydroxyketone, but that the compound  $NH{<}\begin{array}{c}C_6H_4\\ CO\end{array}{>}C\colon N\cdot C_6H_3Me\cdot NHEt$ is first formed which successively yields  $N{<}\begin{array}{c}C_6H_4\\ C(OH)\end{array}{>}C\colon N\cdot C_6H_3Me\cdot NHEt$ and  $\begin{array}{l}C_6H_4\cdot C{=}N\\ N{=}C\cdot NEt\end{array}>C_6H_3Me$. W. A. D.

Study of the *iso*Rosinduline and *iso*Rosindone Reactions. By Otto Fischer (*Ber.*, 1901, **34**, 940—949).—[with G. A. Bruhn]. 10-*Methyl*iso*rosindone hydrochloride*,  $CH{<}\begin{array}{l}C_6H_4\cdot C\cdot N{=}C\cdot CH\colon CMe\\ CH{-}C\cdot NPhCl\colon C\cdot CH\colon C\cdot OH\end{array}$, prepared by mixing together nitroso-*o*-cresol and phenyl-β-naphthylamine in alcoholic hydrochloric acid solution and gently heating the mixture, is precipitated on the addition of water in the form of red, silky needles; the base crystallises from 70 per cent. alcohol in reddish-brown needles having a metallic lustre and melting at 258°; it dissolves in the ordinary organic solvents, but is insoluble in water. The compound is only slightly basic; its salts, although readily crystallisable, being dissociated by water or alcohol. The *hydriodide* and *hydrobromide* crystallise in felted red needles, the *nitrate* and *sulphate* in yellow needles. The *aurichloride* crystallises in red prisms and has an abnormal composition, $(C_{23}H_{16}N_2O)_2,HAuCl_4$; the *platinichloride*, $(C_{23}H_{16}N_2O)_2,H_2PtCl_6$, forms aggregates of orange-red needles; the mercurichloride separates in prisms, the *ferrichloride* crystallises in green leaflets which appear red by transmitted light.

10-*Methylchlorophenylnaphthaphenazonium chloride*, $C_{23}H_{16}N_2Cl_2$, results from the action of phosphorus pentachloride and phosphorus oxychloride on the 10-methyl*iso*rosindone and crystallises from alcohol or ether in reddish-yellow needles; it is readily soluble in water or alcohol, crystallising from the former solvent on the addition of sodium chloride in brownish-red needles. One of the chlorine atoms contained in this compound is readily exchanged for the bromine, iodine, or NO_3

ion, by double decomposition in aqueous or alcoholic solution; the *bromide*, $C_{23}H_{16}N_2ClBr$, obtained by the interaction of potassium bromide, separates in leaflets or brownish-red, acicular crystals, the *iodide* and *nitrate* crystallising in lustrous, green leaflets. The *platini-* and *auri-chlorides* crystallise in orange needles; the *mercurichlorides* and the *double* salts with ferric and zinc chlorides are also described.

10-*Methyl*-9-*phenyl*iso*rosinduline*,



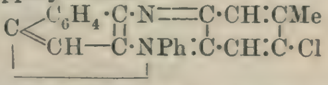
$$\mathrm{CH}\!\left<\begin{array}{l}\mathrm{C_6H_4\cdot C\cdot N{=\!=}C\cdot CH{:}CMe}\\ \mathrm{CH{-}C\cdot NPh{:}C\cdot CH\cdot CNPh}\end{array}\right.,$$

obtained in the form of its *hydrochloride* by heating an alcoholic solution of 10-methylchlorophenylnaphthaphenazonium chloride and aniline (2 mols.), separates from benzene in crystals having a bronzy reflex; the *hydrobromide*, *hydriodide*, and *nitrate* are crystalline, yellow salts.

10-*Methyl*-9-*tolyl*iso*rosinduline*, similarly prepared by substituting *p*-toluidine for aniline in the preceding reaction, separates from dilute alcohol in dark blue crystals and melts at 225°—226°.

10-*Methyl*-9-*β*-*naphthyl*iso*rosinduline* crystallises from benzene in light blue prisms having a grey metallic lustre; its *hydrochloride* crystallises in lustrous, black leaflets, and the *nitrate* separates from alcohol in crystals having a coppery reflex.

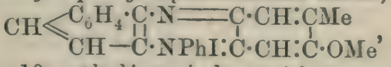
10-*Methyl*-9-*chlororosindone*,



$$\mathrm{C}\!\left<\begin{array}{l}\mathrm{C_6H_4\cdot C\cdot N{=\!=}C\cdot CH{:}CMe}\\ \mathrm{CH{-}C\cdot NPh{:}C\cdot CH{:}C\cdot Cl}\end{array}\right.$$

(compare Abstr., 1900, i, 460), produced by boiling 10-methylchlorophenylnaphthaphenazonium chloride with an aqueous solution of sodium acetate, crystallises from alcohol in orange leaflets with a bronzy reflex, it is soluble in the ordinary organic solvents and sublimes at 300° with partial decomposition; its solution in concentrated sulphuric acid is dichroic, being blue by reflected, and red by transmitted light.

9-*Methoxy*-10-*methyl*-7-*phenylnaphthazonium iodide*,

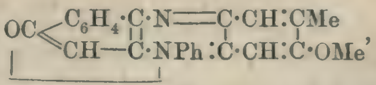


$$\mathrm{CH}\!\left<\begin{array}{l}\mathrm{C_6H_4\cdot C\cdot N{=\!=}C\cdot CH{:}CMe}\\ \mathrm{CH{-}C\cdot NPhI{:}C\cdot CH{:}C\cdot OMe}\end{array}\right.,$$

formed by heating 10-methyl*iso*rosindone with excess of methyl iodide at 100°, crystallises from alcohol in lustrous, green needles; on treatment with nitric acid, it yields the *nitrate* which also separates in green needles.

9-*Ethoxy*-10-*methyl*-7-*phenylnaphthazonium iodide* resembles its lower homologue.

9-*Methoxy*-10-*methylrosindone*,



$$\mathrm{OC}\!\left<\begin{array}{l}\mathrm{C_6H_4\cdot C\cdot N{=\!=}C\cdot CH{:}CMe}\\ \mathrm{CH{-}C\cdot NPh{:}C\cdot CH{:}C\cdot OMe}\end{array}\right.,$$

produced by heating the preceding methoxy-iodide with alcoholic potassium hydroxide, crystallises from alcohol in brownish-red needles melting at 287—288°; its solution in concentrated sulphuric acid is dichroic. These results indicate that the indone produced from nitroso-*o*-cresol is in all respects analogous with *iso*rosindone.

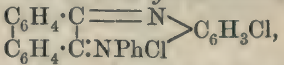
[With M. von Cammerloher.]—The isomeric *methyl*iso*rosindone* obtained in the form of its *hydrochloride* by the interaction of nitroso-*m*-cresol and phenyl-*β*-naphthylamine in alcoholic hydrochloric acid solution, crystallises from dilute alcohol in needles having a bronze reflex; the base is soluble in the ordinary organic solvents but not in water, its salts are dissociated by the latter medium. The *hydriodide* crystallises in green needles, the *hydrobromide* in yellow needles, and the *nitrate* in prisms having a bronze reflex. The *platinichloride* and *mercurichloride* crystallise in red needles.

2-*Nitroso*-1 : 3 : 5-*xylenol* crystallises from alcohol in yellow prisms and melts at 175°; it is insoluble in water but dissolves in the ordinary organic solvents and ammonia solution.

6-*Nitroso*-1 : 2 : 3-*xylenol* crystallises in yellow needles and melts at 166°.

2-*Nitroso*-1 : 3 : 5-*ethylxylidine*, prepared by ethylating *s*-xylidine with ethyl bromide, treating the product with nitrous acid, heating the nitrosoamine with alcoholic hydrochloric acid, and decomposing the yellow *hydrochloride* produced with ammonia, crystallises from benzene in steel-blue prisms and melts at 138°. G. T. M.

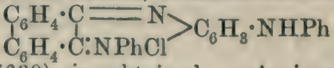
Chloro-derivatives of Azonium Dyes. I. By FRIEDRICH KEHRMANN and WALTHER HIBY (*Ber.*, 1901, **34**, 1085—1095).—5-*Chloro-2-aminodiphenylamine hydrochloride*, prepared from Laubenheimer's 5-chloro-2-nitrodiphenylamine (Abstr., 1876, ii, 294), condenses at the ordinary temperature with phenanthraquinone in glacial acetic acid solution to form 11-*chloroflavinduline chloride*,



$$\begin{array}{l} C_6H_4\cdot C{=\!=\!=}N \\ C_6H_4\cdot C{:}NPhCl \end{array} > C_6H_3Cl,$$

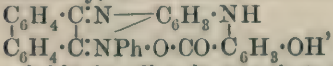
which separates from alcohol in large crystals of the colour of potassium dichromate; the corresponding *nitrate* crystallises from alcohol in blood-red prisms with a greenish lustre. The *base*, $C_{26}H_{16}N_2Cl\cdot OH$, is a yellowish-green powder which cannot be recrystallised owing to decomposition occurring; when heated with acetic anhydride, it yields, not the acetyl derivative of the pseudo-form, but the acetate of the azonium base.

Aromatic bases interact with 11-chloroflavinduline chloride to form compounds identical with those obtained by their direct action on flavinduline. Thus, with aniline, 11-anilinoflavinduline chloride,



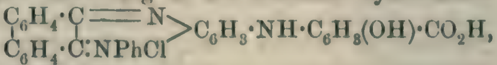
$$\begin{array}{l} C_6H_4\cdot C{=\!=\!=}N \\ C_6H_4\cdot C{:}NPhCl \end{array} > C_6H_3\cdot NHPh$$

(German Patent, 97639), is obtained. *p*-Aminosalicylic acid yields similarly, in alcoholic solution in presence of sodium acetate, the *salt*,



$$\begin{array}{l} C_6H_4\cdot C{:}N{=\!=}C_6H_3\cdot NH \\ C_6H_4\cdot C{:}NPh\cdot O\cdot CO\cdot C_6H_3\cdot OH \end{array},$$

in bluish-black crystals sparingly soluble in all solvents, but dissolving in hot alcoholic hydrochloric acid to form the *chloride*,

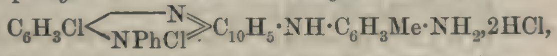


$$\begin{array}{l} C_6H_4\cdot C{=\!=\!=}N \\ C_6H_4\cdot C{:}NPhCl \end{array} > C_6H_3\cdot NH\cdot C_6H_3(OH)\cdot CO_2H,$$

which separates in violet needles.

10-*Chloro*-12-*phenylisonaphthaphenazonium* 12-*nitrate*, prepared by condensing 5-chloro-2-aminodiphenylamine sulphate with β-naphthaquinone and salting out with solid sodium nitrate, crystallises from alcohol in brownish-red granules; with aqueous-alcoholic dimethylamine, it yields 10-dimethylamino-12 phenyl*iso*naphthaphenazonium 12 nitrate (Abstr., 1898, i, 154), whilst with *p*-aminosalicylic acid it forms an internal *salt*, $C_{29}H_{19}O_3N_3$, crystallising in greenish needles and analogous to that obtained similarly from 11-chloroflavinduline.

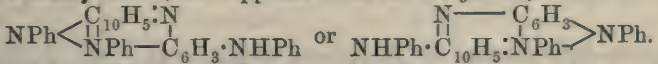
10-*Chlorophenylrosinduline chloride* (10-*chloro*-5-*anilino*-7-*phenylphenazonium* 7-*chloride*), prepared from 5-chloro-2-aminodiphenylamine hydrochloride and 4-anilino-β-naphthaquinone, crystallises from absolute alcohol in dark green prisms; 10-*chloro*-5-p-*tolylrosinduline chloride*, obtained similarly, using 4-toluidino-β-naphthaquinone, crystallises from alcohol in slender needles with a bronzy lustre, whilst 10-*chloro-β-naphthylrosinduline chloride* is a reddish-brown, crystalline powder only sparingly soluble in water and alcohol. 10-*Chloro*-6-m-*amino*-p-*tolylrosinduline chloride dihydrochloride*,



$$C_6H_3Cl{<}\begin{matrix}N\\NPhCl\end{matrix}{\geqslant}C_{10}H_5\cdot NH\cdot C_6H_3Me\cdot NH_2,2HCl,$$

obtained by using *m*-tolylenediamino-β-naphthaquinone, separates from alcohol in crystals with a green, metallic lustre.

When the 10-chlororosindulines are boiled with aromatic bases, the halogen atom is replaced by an amino-radicle, naphthaphenosafranine derivatives being formed. *Diphenylnaphthaphenosafranine chloride* (5 : 9-*dianilino*-7-*phenylnaphthaphenazonium* 7-*chloride*), obtained by using aniline, crystallises from alcohol in granules with a coppery lustre; the derived *base* crystallises from water in greenish needles with a brassy lustre, and appears to be an *anhydride*,

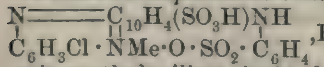


$$NPh{<}\begin{array}{l}C_{10}H_5\!:\!N\\ \|\qquad\quad\ |\\ NPh{-}C_6H_3\cdot NHPh\end{array}\quad\text{or}\quad \begin{array}{l}\qquad\quad\ N{-\!\!-}C_6H_3\\ \qquad\quad\ \|\qquad\ |\\ NHPh\cdot C_{10}H_5\!:\!NPh\end{array}{>}NPh.$$

Di-p-*tolylnaphthaphenosafranine chloride*, prepared from chloro-*p*-tolylrosinduline chloride and *p*-toluidine, separates from boiling alcohol in bronze-coloured crystals, and yields a *base* which forms green crystals from a mixture of benzene and alcohol, and is an anhydride like its lower homologue. W. A. D.

Chloro-derivatives of Azonium Dyes. II. By FRIEDRICH KEHRMANN and H. MÜLLER (*Ber.*, 1901, **34**, 1095—1101).—3-*Chloro*-6-*nitromethylaniline*, prepared by the interaction of 1-chloro-3 : 4-dinitrobenzene and aqueous methylamine in alcoholic solution at the ordinary temperature, crystallises from alcohol in orange-red needles, melts at 104—105°, and on reduction yields 4-*chloro-o-phenylenemethyldiamine*. The *hydrochloride* of this condenses with 4-amino-1 : 2-naphthaquinone in boiling alcoholic solution to form 9-*chloro*-5-*amino*-7-*methylnaphthaphenazonium* 7-*chloride*, which crystallises from alcohol in small, ruby-red prisms with a golden sheen, and shows an intense red fluorescence in alcoholic solution; the *nitrate* forms slender, crimson needles, and the *platinichloride* and *dichromate* garnet-coloured, crystalline powders. With 4-anilino-1 : 2-naphthaquinone, 9-*chloro*-5-*anilino*-7-*methylnaphthaphenazonium chloride* is obtained; it crystallises from alcohol in sheaf-like aggregates of dark-red needles; the *dichromate* and *platinichloride* are dark-red, crystalline powders.

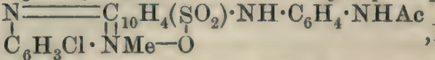
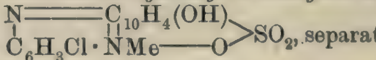
9-*Chloro*-5-*sulphanilino*-7-*methylnaphthaphenazonium*-3-*sulphonic acid*,

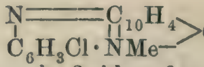


$$\begin{array}{l}N{=\!=\!=\!=}C_{10}H_4(SO_3H)NH\\ |\qquad\qquad\ \|\qquad\qquad\quad\ |\\ C_6H_3Cl\cdot NMe\cdot O\cdot SO_2\cdot C_6H_4\end{array},H_2O,$$

prepared by combining 3-chloro-6-aminomethylaniline hydrochloride with *sodium*-4-*sulphanilino*-1 : 2-

naphthaquinone-6-*sulphonate* (made from sodium sulphanilate and potassium 4 : 6-β-naphthaquinonedisulphonate) in aqueous solution at 100°, and precipitating with hydrochloric acid, forms small, glittering red crystals with a golden lustre.

9-*Chloro*-5-p-*acetylaminoanilino*-7-*methylnaphthaphenazonium*-3-*sulphonic acid*,  $\begin{array}{l}N{=\!=\!=}C_{10}H_4(SO_2)\cdot NH\cdot C_6H_4\cdot NHAc\\ C_6H_3Cl\cdot NMe{-}O\end{array}$,H_2O, obtained similarly from the quinoneanilide prepared from *p*-aminoacetanilide and potassium β-naphthaquinone-4 : 6-disulphonate, separates from glacial acetic acid in violet-brown crystals ; from the mother liquors, on long standing, 10-*chloro*-5-*hydroxy*-12-*methyl*iso*naphthaphenazonium*-3-*sulphonic acid*,  $\begin{array}{l}N{=\!=\!=}C_{10}H_4(OH)\\ C_6H_3Cl\cdot NMe{-}O\end{array}{>}SO_2$, separates as a brownish-red, crystalline powder.

9-*Chloro*-7-*methylrosindone*,  $\begin{array}{l}N{=\!=\!=}C_{10}H_4\\ C_6H_3Cl\cdot NMe{-}\end{array}{>}O$, prepared by leaving 4-hydroxy-β-naphthaquinone and 3-chloro-6-aminomethylaniline in alcoholic solution at the ordinary temperature, crystallises from benzene in garnet-coloured leaflets with a golden lustre ; simultaneously there is formed the isomeric 10-*chloro*-12-*methylprasindone*, which is insoluble in benzene and yields a *chloride* crystallising in lustrous black needles. W. A. D.

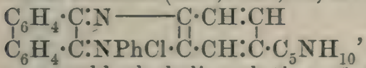
Chloro-derivatives of Azonium Dyes. III. By FRIEDRICH KEHRMANN and S. KRAZLER (*Ber.*, 1901, 34, 1102—1108).—3-*Chloro*-6-*nitrophenyl*-p-*tolylamine*, $NO_2\cdot C_6H_3Cl\cdot NH\cdot C_6H_4Me$, prepared by heating 1-chloro-3 : 4-dinitrobenzene with *p*-toluidine and anhydrous sodium acetate at 100°, crystallises from light petroleum in scarlet needles and melts at 126° ; 3-*chloro*-6-*nitro*-4′-*acetylaminodiphenylamine*, $NO_2\cdot C_6H_3Cl\cdot NH\cdot C_6H_4\cdot NHAc$, obtained similarly, using *p*-aminoacetylanilide, crystallises from alcohol in lustrous, red needles and melts at 221°. On reduction with stannous chloride and alcoholic hydrochloric acid, the foregoing nitro-compounds yield respectively 3-*chloro*-6-*aminophenyl*-p-*tolylamine*, and 3-*chloro*-6 : 4′-*diaminodiphenylamine*.

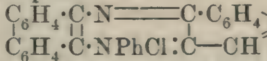
9-*Chlororosinduline chloride* (9-*chloro*-5-*amino*-7-*phenylnaphthaphenazonium* 7-*chloride*), prepared by boiling together 4-amino-1 : 2-naphthaquinone and 3-chloro-6-aminodiphenylamine in alcoholic solution, separates from alcohol, to which it imparts a red fluorescence, in garnet-red crystals ; the *dichromate* is a blood-red, crystalline powder.

9-*Chloro*-5-p-*toluidino*-7-p-*tolylnaphthaphenazonium* 7-*chloride*, prepared by boiling 4-*p*-toluidino-1 : 2-naphthaquinone with 3-chloro-6-aminophenyl-*p*-tolylamine in alcoholic solution, crystallises in aggregates of four-sided prisms with a greenish, metallic lustre ; the derived *base* forms brassy needles, and is the anhydride $C_{30}H_{22}N_3Cl$. On boiling the chloride with *p*-toluidine, the safranine dye, 5 : 9-*di*-p-*toluidino*-7-p-*tolylnaphthaphenazonium chloride*, is obtained in blue crystals with a golden lustre.

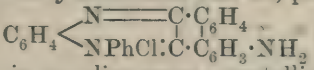
9-*Chloro*-5-*amino*-7-p-*aminophenylnaphthaphenazonium chloride*, prepared from the foregoing 3-chloro-6 : 4′-diaminodiphenylamine and

4-amino-1 : 2-naphthaquinone, crystallises from alcohol, to which it imparts a brownish-red fluorescence, in dark brown crystals with a bronzy lustre; the *dichromate* is a dark brown, crystalline powder. Acetic anhydride at the ordinary temperature acetylates only the amino-group in the 7-phenyl nucleus of the foregoing chloride, the red *acetyl* derivative obtained crystallising from alcohol; on eliminating the unattacked amino-group by the diazo-reaction, and hydrolysing the acetyl derivative so formed, a new *chloroisorosinduline* (9-*chloro*-7-p-*aminophenylnaphthaphenazonium*) is obtained; the *bromide* crystallises from water either in slender, orange-yellow plates, or, when grown more slowly, in thick prisms with a dark green, metallic lustre, and the *dichromate* is a dark brown, crystalline powder. W. A. D.

Nitro- and Amino-flavindulines. By FRIEDRICH KEHRMANN and JOSEF EICHLER (*Ber.*, 1901, **34**, 1210—1217).—11-*Piperidinoflavinduline*,  $\begin{array}{l}C_6H_4{\cdot}C{:}N\text{———}C{\cdot}CH{:}CH\\ C_6H_4{\cdot}C{:}NPhCl{\cdot}C{\cdot}CH{:}C{\cdot}C_5NH_{10}\end{array}$, prepared by the action of piperidine on a cold alcoholic solution of flavinduline chloride, forms dark blue needles with a copper-like lustre; the *dichromate*, $(C_{31}H_{26}N_3)_2Cr_2O_7$, is a blue-green, crystalline precipitate.

Phenanthrarosinduline,  $\begin{array}{l}C_6H_4{\cdot}C{\cdot}N{=\!=}C{\cdot}C_6H_4\\ C_6H_4{\cdot}C{\cdot}NPhCl{:}C{-}CH\end{array}\!\!>\!C{\cdot}NH_2$, prepared by the action of ammonia and air on naphthaflavinduline chloride, crystallises from alcohol in dark red prisms with a bronze-like lustre; the *dichromate*, $(C_{30}H_{20}N_3)_2Cr_2O_7$, forms a dark red, crystalline precipitate. *Phenylphenanthrarosinduline*, $C_{36}H_{24}N_3Cl$, prepared by the action of aniline on naphthaflavinduline, forms large, dark violet crystals with a copper-like lustre.

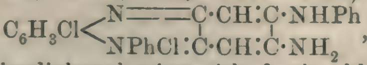
When treated with cold concentrated nitric acid, flavinduline nitrate gives a mixture of nitro-derivatives, of which only one was isolated; this *nitroflavinduline nitrate*, $C_{26}H_{16}N_3O_4$, crystallises from alcohol in glistening, straw-yellow needles, and is reduced by stannous chloride to an *aminoflavinduline chloride*, probably

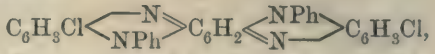


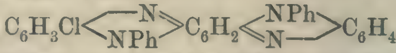
$$C_6H_4<\begin{array}{l}N{=\!=}C{\cdot}C_6H_4\\ NPhCl{:}C{\cdot}C_6H_3{\cdot}NH_2\end{array}\quad [NH_2=7\,?];$$

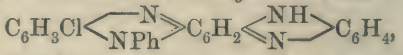
the *dichromate* is an olive-green, crystalline precipitate; the *platinichloride* resembles the dichromate; the aminoflavinduline closely resembles Kehrmann and Kikine's diaminoflavinduline (Abstr., 1900, i, 61) and *iso*rosinduline No. 12 (this vol., i, 101). A second aminoflavinduline is formed on reducing the mother liquors of the nitroflavinduline, which is identical with that previously described (Abstr., 1900, i, 61), and probably contains the amino-group in the 3-position.

T. M. L.

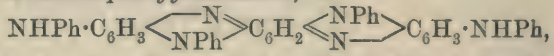
Fluorindine. By FRIEDRICH KEHRMANN and BERNHARD GUGGENHEIM (*Ber.*, 1901, **34**, 1217—1224).—*Chloroanilinoaposafranine chloride*,  $C_6H_3Cl<\begin{array}{l}N{=\!=}C{\cdot}CH{:}C{\cdot}NHPh\\ NPhCl{:}C{\cdot}CH{:}C{\cdot}NH_2\end{array}$, is produced by oxidation of chloroaminodiphenylamine with ferric chloride; it was prepared by Ernst (Abstr., 1891, 299), but not analysed; it crystallises from alcohol in greenish needles with a metallic lustre, whilst the *base* separates in black, glistening tablets.

Dichlorodiphenylfluorindine,  $C_6H_3Cl<\genfrac{}{}{0pt}{}{N}{NPh}>C_6H_2<\genfrac{}{}{0pt}{}{NPh}{N}>C_6H_3Cl$, prepared by heating the preceding compound with Laubenheimer's diamine and benzoic acid, crystallises in violet-grey needles; the *hydrochloride* crystallises in needles with a brass-like lustre, and the *dihydrochloride* in copper coloured scales.

Chlorodiphenylfluorindine,  $C_6H_3Cl<\genfrac{}{}{0pt}{}{N}{NPh}>C_6H_2<\genfrac{}{}{0pt}{}{NPh}{N}>C_6H_4$, prepared by condensing the aposafranine chloride with *o*-aminodiphenylamine, crystallises from nitrobenzene or ethyl benzoate, forms red-violet needles with a metallic lustre, and melts above 360°; it forms a copper-red *dihydrochloride*, and a brass-like *monohydrochloride*.

Chlorophenylfluorindine,  $C_6H_3Cl<\genfrac{}{}{0pt}{}{N}{NPh}>C_6H_2<\genfrac{}{}{0pt}{}{NH}{N}>C_6H_4$, prepared by condensing the aposafranine chloride with *o*-phenylenediamine, is a dark red, crystalline powder; the *monohydrochloride* crystallises from alcohol in green needles with a metallic lustre; the base does not appear to give a dihydrochloride.

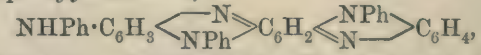
3 : 10-*Dianilinodiphenylfluorindine*,



$$NHPh\cdot C_6H_3<\genfrac{}{}{0pt}{}{N}{NPh}>C_6H_2<\genfrac{}{}{0pt}{}{NPh}{N}>C_6H_3\cdot NHPh,$$

prepared by heating dichlorodiphenylfluorindine hydrochloride with aniline and aniline hydrochloride crystallises from a mixture of alcohol and benzene; the *hydrochloride*, $C_{42}H_{30}N_6,HCl$, crystallises from alcohol in flakes with a bronze-like lustre.

3-*Anilinodiphenylfluorindine*,

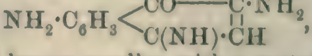


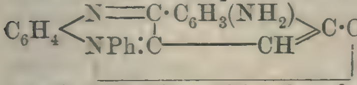
$$NHPh\cdot C_6H_3<\genfrac{}{}{0pt}{}{N}{NPh}>C_6H_2<\genfrac{}{}{0pt}{}{NPh}{N}>C_6H_4,$$

prepared by the action of aniline and aniline hydrochloride on chlorodiphenylfluorindine hydrochloride, crystallises from a mixture of alcohol and benzene in dark blue flakes with a green lustre; the *hydrochloride* crystallises from alcohol, in which it is less soluble than the hydrochloride of the dianilino-base.

Nitrodiphenylfluorindine, $C_{30}H_{19}N_4\cdot NO_2$, prepared by adding the theoretical quantity of potassium nitrate to a solution of diphenylfluorindine in sulphuric acid, is a greenish-grey, crystalline powder soluble in boiling nitrobenzene.

Nitrophenylfluorindine, $C_{24}H_{15}N_4\cdot NO_2$, prepared in a similar manner from phenylfluorindine, forms minute, brown-red scales with a golden lustre. T. M. L.

Constitution of *iso*Rosinduline No. 8. Derivatives of Trinitro-α-naphthol [$OH\colon(NO_2)_3 = 1:2:4:8$]. By FRIEDRICH KEHRMANN and EMILE MISSLIN (*Ber.*, 1901, **34**, 1224—1233).—By reducing 2 : 4 : 8 trinitro-1-naphthol, and then oxidising by means of a current of air, 2 : 8-*diamino*-1 : 4-*naphthaquinoneimine*,  $NH_2\cdot C_6H_3<\genfrac{}{}{0pt}{}{CO-C\cdot NH_2}{C(NH)\cdot CH}$, is produced; the *hydrochloride* forms red-brown needles with a metallic lustre. By heating with ammonia, the quinoneimine is converted into diamino-α- and β-naphthaquinones, whilst sodium hydroxide gives 8-*amino-2-hydroxy*-1 : 4-*naphthaquinone*, which crystallises from alcohol in dark brown needles with a green, metallic lustre, and begins to sublime with partial decomposition at 225°; the *acetyl* derivative of the quinone crystallises from water in dark brown, glistening needles, and sublimes with partial decomposition at 200°. 1-*Aminorosindone*,



$C_6H_4<\begin{matrix}N{=}C\cdot C_6H_3(NH_2)\\ NPh{:}C\text{———}CH\end{matrix}>C\cdot O$, prepared by condensing the preceding acetyl derivative with phenyl-*o*-phenylenediamine, crystallises from alcohol in dark red needles with a brass-like lustre, and gives an *acetyl* derivative which crystallises in red-brown flakes and sublimes at 300°; this acetyl derivative can also be prepared from *iso*rosinduline No. 8 (Abstr., 1900, i, 60) by acetylation and subsequent oxidation, and the latter is thus shown to be a 1-aminophenylnaphthaphenazonium salt.

The two diaminonaphthaquinones obtained by the action of ammonia on 2 : 8-diamino-1 : 4-naphthaquinoneimine can be separated by reducing to the quinols, converting into tetracetates, and then by hydrolysis and oxidation into diacetylaminoquinones. 4 : 8-*Diacetylamino*-1 : 2-*naphthaquinone* is soluble in alcohol, crystallises from acetic acid in glistening, brownish-yellow flakes, and melts at 225°.

4 : 8-*Diacetylamino*-1 : 4-*naphthaquinone* is insoluble in alcohol, but crystallises from acetic acid in glistening, red flakes, and melts and decomposes at 240—245°. It condenses with *o*-phenylenediamine to 1 : 5-*diacetylaminonaphthaphenazine*, $C_6H_4<\begin{matrix}N\\ N\end{matrix}>C_{10}H_4(NHAc)_2$, which crystallises from nitrobenzene in minute, golden-yellow needles; 1 : 5-*diaminonaphthaphenazine*, $C_{16}H_{12}N_4$, crystallises from nitrobenzene in yellowish-red needles with a brass-like lustre. T. M. L.

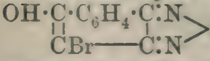
Action of 2 : 3-Dibromo-α-naphthaquinone on *o*-, *m*-, and *p*-Phenylenediamine and some new Derivatives of αβ-Naphthaphenazine. By S. Lindenbaum (*Ber.*, 1901, **34**, 1050—1060).—2-*Bromo-α-naphthaquinone*-3-p-*phenylenediamine*,

$$C_{10}H_4O_2Br\cdot NH\cdot C_6H_4\cdot NH_2,$$

obtained by the action of dibromonaphthaquinone on an alcoholic solution of *p*-phenylenediamine and sodium ethoxide, crystallises from alcohol in deep blue, lustrous plates, is sparingly soluble in ether, light petroleum, or benzene, but more readily in hot alcohol or glacial acetic acid, and does not melt below 350°; it dissolves in sulphuric acid with formation of bromohydroxynaphthaquinone.

2-*Bromo-α-naphthaquinone*-3-m-*phenylenediamine* crystallises from alcohol in copper-coloured, lustrous plates and melts at 194—195°; its solubilities and behaviour with sulphuric acid resemble those of the *p*-compound.

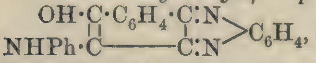
6-*Bromo*-5-*hydroxy*-*αβ*-*naphthaphenazine* (6-*bromo-α-naphtheurhodole*),



$\begin{matrix}OH\cdot C\cdot C_6H_4\cdot C{:}N\\ CBr\text{——}C{:}N\end{matrix}>C_6H_4$, is obtained by the action of dibromonaphthaquinone on *o*-phenylenediamine in presence of potassium ethoxide as a red, amorphous substance, which is insoluble in the usual organic solvents, but crystallises from phenol in red, lustrous scales, and decomposes at about 230°; its *sodium* and *silver* salts are described. The *acetyl* derivative crystallises in yellow, silky needles, and melts at 221°; the *ethyl ether* forms yellow needles and melts at 173°.

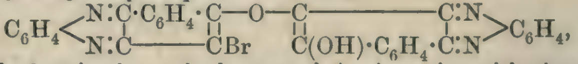
When bromohydroxynaphthaphenazine is heated with benzyl chloride and sodium ethoxide, a compound, $C_{16}H_{10}ON_2$, is produced, which appears to be identical with that obtained from β-naphtheurhodole by Zincke (Abstr., 1893, i, 357) and regarded by him as an 'insoluble modification' of the eurhodole. By the action of nitric acid, bromohydroxynaphthaphenazine is converted into 5 : 6-diketonaphthaphenazine (naphthaphenazine-β-quinone), and when treated with phenol and sulphuric acid yields 5-hydroxynaphthaphenazine (α-naphtheurhodole).

6-*Anilino-5-hydroxy-αβ-naphthaphenazine* (6-*anilino-α-naphtheurhodole*),



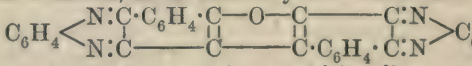
$\begin{matrix}OH\cdot C\cdot C_6H_4\cdot C{:}N \\ NHPh\cdot C\text{———}C{:}N\end{matrix}\!>\!C_6H_4$, obtained by the action of aniline on bromohydroxynaphthaphenazine, crystallises in red needles or leaflets, melts at 210—220°, is soluble in benzene, toluene, or glacial acetic acid, and dissolves in alcoholic alkali with formation of a violet solution; its *diacetyl* derivative melts at 226°.

Bromohydroxydinaphthaphenazine oxide,



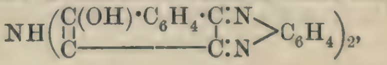
$$C_6H_4\!<\!\begin{matrix}N{:}C\cdot C_6H_4\cdot C\text{—}O\text{—}C\text{————}C{:}N \\ N{:}C\text{———}CBr\quad C(OH)\cdot C_6H_4\cdot C{:}N\end{matrix}\!>\!C_6H_4,$$

obtained by heating bromohydroxynaphthaphenazine with nitrobenzene, crystallises in brownish-violet needles, and melts at 300°; when heated with sodium ethoxide, it is instantly converted into *dinaphthaphenazinefuran*,

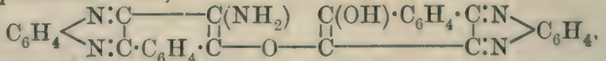


$C_6H_4\!<\!\begin{matrix}N{:}C\cdot C_6H_4\cdot C\text{—}O\text{—}C\text{———}C{:}N \\ N{:}C\text{———}C\text{———}C\cdot C_6H_4\cdot C{:}N\end{matrix}\!>\!C_6H_4$, which crystallises from hot nitrobenzene in greenish-yellow needles, and melts above 300°.

When bromohydroxynaphthaphenazine is heated with alcoholic ammonia, it yields a substance which is either dihydroxydinaphthaphenazineimide,



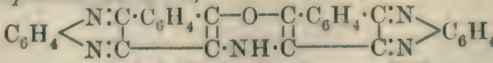
$NH\left(\begin{matrix}C(OH)\cdot C_6H_4\cdot C{:}N \\ C\text{————————}C{:}N\end{matrix}\!>\!C_6H_4\right)_2$, or *aminohydroxydinaphthaphenazine oxide*,



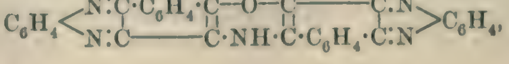
$$C_6H_4\!<\!\begin{matrix}N{:}C\text{———}C(NH_2)\quad C(OH)\cdot C_6H_4\cdot C{:}N \\ N{:}C\cdot C_6H_4\cdot C\text{—}O\text{—}C\text{————————}C{:}N\end{matrix}\!>\!C_6H_4,$$

but more probably the latter; it crystallises in olive-green needles which contain $1H_2O$ and become blue when heated; it does not melt below 300°. The same compound is produced by the action of alcoholic ammonia on anilinohydroxynaphthaphenazine. The *ethyl* derivative, $NEt(C_{16}H_8N_2\cdot OH)_2$ or $NHEt\cdot C_{16}H_8N_2\cdot O\cdot C_{16}H_8N_2\cdot OH$, obtained by heating the bromophenazine with alcoholic ethylamine, is an olive-green amorphous substance.

Dinaphthaphenazineoxazine,



$$C_6H_4\!<\!\begin{matrix}N{:}C\cdot C_6H_4\cdot C\text{—}O\text{—}C\cdot C_6H_4\cdot C{:}N \\ N{:}C\text{———}C\cdot NH\cdot C\text{————}C{:}N\end{matrix}\!>\!C_6H_4 \text{ or}$$



$$C_6H_4\!<\!\begin{matrix}N{:}C\cdot C_6H_4\cdot C\text{—}O\text{—}C\text{———}C{:}N \\ N{:}C\text{———}C\cdot NH\cdot C\cdot C_6H_4\cdot C{:}N\end{matrix}\!>\!C_6H_4,$$

produced when either of the two substances described in the last paragraph is heated with nitrobenzene or glacial acetic acid, crystallises in lustrous, dark-blue needles, and melts above 300°. E. G.

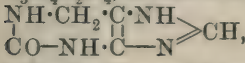
Reaction between Substituted Aminobenzophenones and Aromatic Amines in presence of Sulphuric Acid. By PAUL LEMOULT (*Compt. rend.*, 1901, **132**, 885—888).—When tetramethyl-*p*-diaminobenzophenone and diphenylamine interact in presence of sulphuric acid, tetramethylphenyl-*p*-triaminotriphenylmethanesulphonic acid is obtained in almost theoretical quantity. A similar result is obtained with the tertiary methyl, ethyl, benzyl, and other substitution derivatives of diphenylamine, and with its homologues, such as phenyl-*p*-tolylamine or phenyl-*o*-tolylamine, but not with *p*-ditolylamine, or with any secondary or tertiary amine containing only one benzene nucleus. Phenyl-α-naphthylamine, phenyl-β-naphthylamine, *o*-tolyl-β-naphthylamine, and methylphenyl-β-naphthylamine give the reaction, but not *p*-tolyl-α-naphthylamine, *p*-tolyl-β-naphthylamine, or αβ-dinaphthylamine.

In order that the condensation may take place it is essential that the amine contain at least one phenyl group, and that the para-position in the latter be unoccupied. The same condensation takes place between tetraethyl-*p*-diaminobenzophenone and diphenylamine, ethyldiphenylamine, phenyl-α-naphthylamine, and phenyl-β-naphthylamine, but not with *p*-ditolylamine, *p*-tolyl-α-naphthylamine, *p*-tolyl-β-naphthylamine, α-dinaphthylamine, β-dinaphthylamine, ethylaniline, and diethylaniline, or benzylaniline. Sulphonation of the benzophenone does not affect the reaction, although it has some influence on the exact colour of the product.

Dimethylaminobenzophenone and its sulphonic acid undergo a similar condensation, subject to the same limitations, and the products will be described subsequently.

It will be seen that the condensation in presence of sulphuric acid is less general than in presence of phosphorus oxychloride, since in the latter case the nature of the amine has comparatively little influence on the occurrence and progress of the reaction. C. H. B.

Electrolytic Reduction of Xanthine. By JULIUS TAFEL and BENNO ACH (*Ber.*, 1901, **34**, 1165—1169. Compare this vol., i, 106).—Xanthine, $C_5H_4O_2N_4$, is converted by electrolytic reduction into deoxyxanthine,

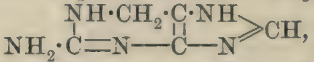


$$\begin{matrix} NH\cdot CH_2\cdot C\cdot NH \\ | \qquad\qquad \| \qquad \\ CO-NH\cdot C-\!\!-N \end{matrix}\!\!>\!CH,$$

the yield being nearly quantitative when the reduction is carried out in 75 per cent. sulphuric acid below 12°. It crystallises with $1H_2O$ in needles, and is deposited from supersaturated solutions as an anhydrous granular powder, which gradually takes up water at 25° and is reconverted into needles. When heated above 250°, it gradually decomposes without melting. In general properties, it closely resembles the methyldeoxyxanthines and is probably 5-oxy-6 : 7-dihydropurine.

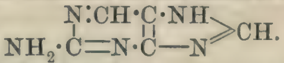
It is oxidised by silver nitrate, probably with formation of 5-hydroxypurine, and is also oxidised by potassium permanganate and lead peroxide. It dissolves in both acids and alkalis, the acid solutions being easily decomposed by heat. *Deoxyxanthine sulphate* crystallises in colourless needles, the *nitrate* is a granular, crystalline powder, and the *picrate* crystallises in yellow, anhydrous needles. Phosphotungstic acid, phosphomolybdic acid, and copper sulphate all produce precipitates. A. H.

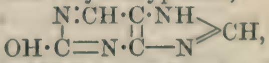
Reduction Products of Guanine. By JULIUS TAFEL and BENNO ACH (*Ber.*, 1901, **34**, 1170—1181. Compare the foregoing abstract).—Guanine, $C_5H_5ON_5$, is converted by electrolytic reduction in solution in 60 per cent. sulphuric acid into *deoxyguanine*,



$$\begin{array}{l}\qquad NH\cdot CH_2\cdot C\cdot NH \\ NH_2\cdot C{=}N{-}C{-}N\end{array}\!\!>CH,$$

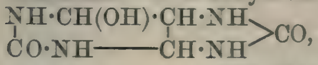
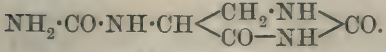
which crystallises in microscopic needles, and melts and decomposes at 204°. It is a strong base, which combines with atmospheric carbon dioxide and forms salts, both with one and two equivalents of mineral acids. The normal *sulphate*, $(C_5H_7N_5)_2,H_2SO_4$, crystallises with $1H_2O$ in granules, and when anhydrous melts and decomposes at 267°. The *hydrogen sulphate*, $C_5H_7N_5,H_2SO_4$, crystallises in yellowish, anhydrous prisms. The *normal hydrochloride* crystallises in tablets and dissolves in 16·9 parts of water at 0°. The solution gives precipitates with the usual reagents for basic substances. The acid hydrochloride has not been prepared pure. *Deoxyguanine acetate*, $C_5H_7N_5,C_2H_3O_2$, crystallises in prisms, and melts and decomposes at about 222°. The *picrate* crystallises in orange yellow rhombohedra.

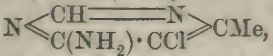
Deoxyguanine is converted by oxidation, which is best carried out by the action of bromine on the acetate in presence of acetic acid, into 5-*aminopurine*,  $\begin{array}{l}\qquad N{:}CH\cdot C\cdot NH \\ NH_2\cdot C{=}N\cdot C{-}N\end{array}\!\!>CH$. The base crystallises with $1H_2O$ in spherical aggregates, and is more readily soluble than the isomeric adenine, which it closely resembles in its general properties. It yields precipitates with mercuric chloride, phosphomolybdic acid, and cadmium chloride. It gives no colour reaction on exposure to air after treatment with zinc and hydrochloric acid, and can thus be readily distinguished from adenine. The base is soluble both in acids and alkalis; the *sulphate* is more readily soluble than adenine sulphate, the *nitrate* is sparingly soluble, the *platinichloride* is an amorphous precipitate, the *oxalate* crystallises in needles or granules, and the *picrate* crystallises without water in yellow needles. Nitrous acid converts aminopurine into 5-hydroxypurine,



$$\begin{array}{l}\qquad N{:}CH\cdot C\cdot NH \\ OH\cdot C{=}N\cdot C{-}N\end{array}\!\!>CH,$$

which crystallises with $1H_2O$ in needles, becomes anhydrous at 122°, and dissolves in 22 parts of boiling water. On exposure to air after treatment with zinc and hydrochloric acid, followed by excess of alkali, it yields a red coloration similar to that produced by adenine and hypoxanthine. Baryta dissolves the compound at first, but the *barium* salt soon separates. The *nitrate* crystallises in hair-like needles; silver nitrate produces a gelatinous precipitate. A. H.

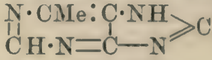
Tetrahydrouric Acid. By JULIUS TAFEL (*Ber.*, 1901, **34**, 1181—1184. Compare this vol., i, 236).—Tetrahydrouric acid is converted by excess of aqueous baryta at 150° into αβ-diaminopropionic acid. This confirms the view expressed previously, that the constitution of tetrahydrouric acid is not indicated by the formula  $\begin{array}{l}NH\cdot CH(OH)\cdot CH\cdot NH \\ CO\cdot NH\text{———}CH\cdot NH\end{array}\!\!>CO$, but more probably by the formula  $NH_2\cdot CO\cdot NH\cdot CH\!<\!\begin{array}{l}CH_2\cdot NH \\ CO\text{—}NH\end{array}\!\!>CO$. The properties of αβ-diaminopropionic acid were found, in some cases, to differ from those described by Klebs (Abstr., 1893, i, 686), the experiments being carried out with acid prepared by his method. The nitrate melts and decomposes at 191—193° (Klebs, 170°), and the dibenzoyl derivative melts at 188—189° (Klebs, 195—197°). A. H.

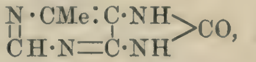
Syntheses in the Purine Group. By Siegmund Gabriel and James Colman (*Ber.*, 1901, **34**, 1234—1257).—5-*Chloro*-6-*amino*-4-*methylpyrimidine*,  $N\!\lessgtr\!\begin{array}{l}CH\text{=====}N \\ C(NH_2)\cdot CCl\end{array}\!\!>CMe$, prepared by the action of chlorine on 6-amino-4-methylpyrimidine (Abstr., 1900, i, 55), crystallises from water in stout prisms, sinters at 195°, melts at 197—198°, volatilises slowly above 100°, and dissolves readily in acids and in hot alcohol or ether. The corresponding *bromo*-compound crystallises from hot water in long needles, melts at 197°, sublimes slowly at 100°, and gives a *platinichloride* which crystallises in orange-yellow needles.

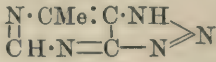
6-*Nitroamino*-4-*methylpyrimidine*, $C_4N_2H_2Me\cdot NH\cdot NO_2$, prepared by the action of nitric acid on methylaminopyrimidine, crystallises from water in flat, colourless prisms, and on reduction is usually reconverted into methylaminopyrimidine. When reduced with zinc dust and acetic acid in presence of ice, it gives 6-*hydrazino*-4-*methylpyrimidine*, $C_4N_2H_2Me\cdot NH\cdot NH_2$, which crystallises from ethyl acetate in colourless needles, melts at 138—140·5°, reduces Fehling's solution, and distils without decomposition.

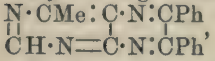
6-*Nitroamino*-2-*chloro*-4-*methylpyrimidine*, $C_4N_2HMeCl\cdot NH\cdot NO_2$, prepared by the action of nitric acid on 6-amino-2-chloro-4-methylpyrimidine, crystallises in minute needles, volatilises slowly at 100°, explodes on heating, and is reduced by hydrogen iodide and phosphorus to 6-amino-4-methylpyrimidine.

2 : 6-*Dichloro*-5-*nitro*-4-*methylpyrimidine*, $C_4N_2MeCl_2\cdot NO_2$, could not be obtained by nitrating dichloromethylpyrimidine, but was prepared by heating nitromethyluracil with phosphorus oxychloride at 155—160° in sealed tubes; it distils at 240°, crystallises from light petroleum or from alcohol in stout prisms, and melts at 53—54·5°. 2-*Chloro*-5-*nitro*-6-*amino*-4-*methylpyrimidine*, $NO_2\cdot C_4N_2MeCl\cdot NH_2$, prepared by the action of alcoholic ammonia on the preceding compound, crystallises from alcohol in flat, reddish needles and melts at 170—171°. 2-*Chloro*-5 : 6-*diamino*-4-*methylpyrimidine*, $C_4N_2MeCl(NH_2)_2$, prepared by reducing the preceding compound with stannous chloride, crystallises from hot water in flat, glassy needles, melts at 250°, and forms a crystalline platinichloride; reduction with hydriodic acid gives 5 : 6-*diamino*-4-*methylpyrimidine*, $C_4N_2HMe(NH_2)_2$, which crystallises from acetone in stout columns, melts at 208—209° and boils without decomposition at

325—330°; the *platinichloride* forms square tablets, and the *hydriodide* colourless prisms. The *formyl* derivative, $NH_2\cdot C_4N_2HMe\cdot NH\cdot CHO$, crystallises from alcohol in flat needles, and when heated above 200° is converted into 7-*methylpurine*,  $\begin{array}{l} N\cdot CMe\colon C\cdot NH \\ \| \qquad\quad\;\; | \\ CH\cdot N{=}C{-}N \end{array}\!\!>\!CH$, which sublimes readily, crystallises from toluene in silky needles, melts at 235—236°, and dissolves both in acids and alkalis; the *potassium* salt forms minute needles, the *picrate* is a crystalline powder, and the *platinichloride* forms yellow needles.

2-*Oxy*-7-*methylpurine*,  $\begin{array}{l} N\cdot CMe\colon C\cdot NH \\ \| \qquad\quad\;\; | \\ CH\cdot N{=}C\cdot NH \end{array}\!\!>\!CO$, prepared by heating diaminomethylpyrimidine with carbamide at 170°, crystallises from alcohol in minute, snow-white needles, dissolves in hot water, and has no acid properties; the *hydrochloride* crystallises in needles, sinters at 325°, melts with frothing at about 345°, and is only slightly soluble in strong hydrochloric acid; the *aurichloride* forms golden-yellow needles or flat prisms. 2-*Thio*-7-*methylpurine*, prepared by heating diaminomethylpyrimidine with thiocarbamide, forms a colourless, crystalline powder, dissolves in ammonia and in alkalis, and volatilises on heating.

4-*Methyl*-5 : 6-*aziminopyrimidine*,  $\begin{array}{l} N\cdot CMe\colon C\cdot NH \\ \| \qquad\quad\;\; | \\ CH\cdot N{=}C{-}N \end{array}\!\!>\!N$, prepared by the action of nitrous acid on diaminomethylpyrimidine, crystallises from hot water in colourless, microscopic needles, sinters at 160° and melts at 174° to a red liquid.

By heating diaminomethylpyrimidine with benzil at 170°, the *azine*,  $\begin{array}{l} N\cdot CMe\colon C\cdot N\colon CPh \\ \| \qquad\quad\;\; | \qquad | \\ CH\cdot N{=}C\cdot N\colon CPh \end{array}$, is formed; it crystallises from hot alcohol in yellow prisms, sinters at about 180° and melts at 184°.

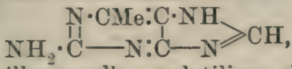
2 : 6-Dichloro-5-nitro-4-methylpyrimidine is reduced by boiling with zinc dust and water to 2-*chloro*-5-*amino*-4-*methylpyrimidine*,

$$C_4N_2HMeCl\cdot NH_2,$$

which melts at 92° and separates from water in felted needles. Sodium methoxide converts it into 5-*amino*-2-*methoxy*-4-*methylpyrimidine*, $OMe\cdot C_4N_2HMe\cdot NH_2$, which melts at 88—89·5°, and has an odour suggestive of lobsters. 5-*Amino*-4-*methylpyrimidine*, $C_4N_2H_2Me\cdot NH_2$, prepared by reducing the chloro-derivative with hydriodic acid, separates from benzene in flat crystals, melts at 152—153°, and boils at about 260°; it forms a *hydrochloride*, a *platinichloride* crystallising in oblong prisms, and an *aurichloride* crystallising in flat needles. 2 : 5-*Diamino*-4-*methylpyrimidine*, $C_4N_2HMe(NH_2)_2$, prepared by heating 2-chloro-5-amino-4-methylpyrimidine with alcoholic ammonia at 200—215°, crystallises from ethyl acetate in short prisms, melts at 183—184°, and is a weaker base than the two isomerides.

2 : 6-*Diamino*-4-*methylpyrimidine*, formed as a bye-product in the action of ammonia on 2 : 6-dichloro-4-methylpyrimidine (Abstr., 1900, i, 54), crystallises from water in clear needles with $1H_2O$, and from acetone in glassy needles containing acetone; it melts at 183—185° and boils at 305—308°.

5-*Nitro*-2 : 6-*diamino*-4-*methylpyrimidine*, $NO_2\cdot C_4N_2Me(NH_2)_2$, prepared by the action of nitric and sulphuric acids on the preceding compound, crystallises from acetic acid, alcohol, or water, forms yellow prisms or needles, melts at 232—233°, and can also be prepared by the action of ammonia on 2 : 6-dichloro-5-nitro-4-methylpyrimidine. It is reduced by stannous chloride to 2 : 5 : 6-*triamino-4-methylpyrimidine*, $C_4N_2Me(NH_2)_3$, which crystallises from water in colourless, glistening needles, from alcohol in stout prisms or rhombohedra, melts at 243°, and reduces Fehling's solution ; the *hydrochloride* crystallises in needles, the *platinichloride* in flat, lemon-yellow prisms, and the *picrate* forms a crystalline powder. The *formyl* derivative forms minute, felted needles, and when heated at 300° is converted into 5-*amino-7-methylpurine*,



$$\begin{array}{l} \qquad\quad N\cdot CMe{:}C\cdot NH \\ NH_2\cdot C\text{——}N{:}C\text{——}N \end{array} \!\!> CH$$

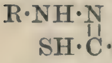
which crystallises from water in felted, silky needles, volatilises when heated on a watch glass, melts above 300° when heated in a capillary tube, and gives a crystalline *hydrochloride*, *platinichloride*, *aurichloride*, *dichromate*, *ferrocyanide*, and *picrate*. T. M. L.

Reduction of Nitro-azo-colouring Matters. By AUGUSTE ROSENSTIEHL (*Compt. rend.*, 1901, **132**, 985—988).—The substantive colouring matter produced by the action of diazotised *m*-azoxy-*o*-toluidine on 1-naphthol-4-sulphonic acid is more conveniently prepared by reducing 4-nitrotoluene-2-azo-1-naphthol-4-sulphonic acid in an alkaline solution by means of stannous oxide, arsenious acid, formaldehyde, or dextrose, the yield obtained by the use of the last of these reagents being quantitative. During reduction, the temperature must be kept below 60°, otherwise an azodiamine is produced. 3-*Azo-2-toluidine*, $N_2(C_6H_3Me\cdot NH_3)_2$, prepared in this manner, crystallises from alcohol, ether, or benzene in brown needles, and melts at 218—220°. G. T. M.

Oxidation of Symmetrical Secondary Benzylhydrazines to Hydrazones. By THEODOR CURTIUS and H. PAULI (*Ber.*, 1901, **34**, 847—853).—o-*Chlorobenzaldazine*, $C_6H_4Cl\cdot CH{:}N\cdot N{:}CH\cdot C_6H_4Cl$, crystallises from alcohol in glistening, yellow needles and melts at 143·5°. It is reduced by sodium amalgam to s-*di*-o-*chlorobenzylhydrazine*, $N_2H_2(CH_2\cdot C_6H_4Cl)_2$, which crystallises from alcohol in small, colourless needles and melts at 86—87°; the hydrochloride, $C_{14}H_{14}N_2Cl_2,HCl$, crystallises from dilute hydrogen chloride in glistening, colourless needles and melts at 169°; the *picrate* forms glistening, yellow needles, and melts and decomposes at 144° ; the *diacetyl* derivative, $C_{18}H_{18}O_2N_2Cl_2$, separates from alcohol in colourless crystals and melts at 102° ; the *dibenzoyl* derivative, $C_{28}H_{22}O_2N_2Cl_2$, separates from alcohol in hard crystals and melts at 118°. The *dinitroso*-derivative, $N_2(NO)_2(CH_2\cdot C_6H_4Cl)_2$, separates from ether as a yellow, crystalline mass and melts at 50—51° ; by warming with alcohol, it is converted into o-*chlorobenzylidenenitroso*-o-*chlorobenzylhydrazine*, $C_6H_4Cl\cdot CH_2\cdot N(NO)\cdot N{:}CH\cdot C_6H_4Cl$, which separates in yellow needles and melts and decomposes at 100—101°. o-*Chlorobenzylhydrazine hydrochloride*, $C_6H_4Cl\cdot CH_2\cdot NH\cdot NH_2,HCl$, prepared by hydrolysing the preceding compound with dilute hydrogen chloride, separates from alcohol in colourless, glistening crystals and melts at 146°; it condenses with *o*-chlorobenzaldehyde in presence of a few drops of sulphuric acid to form *o-chlorobenzylidene-o-chlorobenzylhydrazine*, $C_6H_4Cl{\cdot}CH_2{\cdot}NH{\cdot}N{:}CH{\cdot}C_6H_4Cl$, which crystallises from alcohol in small, yellow needles and melts at 83—84°. *Nitroso-o-chlorobenzylhydrazine*, $C_6H_4Cl{\cdot}CH_2{\cdot}N(NO){\cdot}NH_2$, crystallises from warm water or from dilute alcohol in glistening, colourless flakes and melts at 57°; it condenses with *o*-chlorobenzaldehyde to form *o*-chlorobenzylidenenitroso-*o*-chlorobenzylhydrazine, and with benzaldehyde to *benzylidenenitroso-o-chlorobenzylhydrazine*, $C_6H_4Cl{\cdot}CH_2{\cdot}N(NO){\cdot}N{:}CH{\cdot}C_6H_5$, which separates from alcohol in small, yellow crystals and melts and decomposes at 85—86°; the *acetyl* derivative, $C_{16}H_{14}ON_2Cl_2$, of the preceding compound separates from alcohol in colourless tablets and melts at 110°.

T. M. L.

Stereoisomerism of the Hydrazones of the Esters of Dithiocarbonic Acid. By MAX BUSCH (*Ber.*, 1901, **34**, 1119—1127. Compare Busch and Lingenbrink, Abstr., 1900, i, 66, 411).—The esters of phenyldithiocarbazinic acid, $NHPh{\cdot}NH{\cdot}CS{\cdot}SR$, when acted on by alkali, undergo intramolecular change into hydrazones of dithiocarbonic acid, $NHPh{\cdot}N{:}C(SH){\cdot}SR$, which are readily converted into the corresponding dialkyl esters, $NHPh{\cdot}N{:}C(SR){\cdot}SR'$. When R and R′ are different radicles, these compounds should, in the light of Hantzsch's theory, exist in two stereoisomeric modifications. Such esters have now been obtained crystalline, and it is found that the two stereoisomerides can be obtained by varying the order in which the radicles R and R′ are introduced into the compounds. Since the esters of carbazinic acid pass readily into diazole derivatives, it is assumed that the thialkyl group in them occupies the anti-position, thus:



$$\begin{array}{l} R{\cdot}NH{\cdot}N \\ \qquad\quad \| \\ \quad SH{\cdot}C{\cdot}SR' \end{array}.$$

The stereoisomeric hydrazones show no differences in their chemical behaviour, whilst the solubilities and melting points are approximately the same; the crystalline forms and the colours differ, however, to such an extent as to make it quite easy to recognise and separate any pair of isomerides. The separate isomerides are not readily converted one into the other, although such conversion can be brought about by long continued heating above the melting point; in general, equilibrium is attained after about an hour's heating, a mixture of the two forms being in all cases obtained.

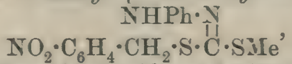
p-Nitrobenzyl phenyldithiocarbazinate,

$$NHPh{\cdot}NH{\cdot}CS{\cdot}S{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2,$$

obtained by the action of the potassium salt on *p*-nitrobenzyl chloride, melts at 134° and crystallises from alcohol in faintly yellow, stout needles, from a mixture of benzene and light petroleum in small, white needles, and from chloroform in stout prisms; it is soluble in ether and to a very slight extent in light petroleum. Its alcoholic solution is turned red or brownish-red by alkali hydroxide or carbonate. Together with the above compound, a small quantity of the *phenylhydrazone* of *di-p-nitrobenzyl dithiocarbonate*, $NHPh{\cdot}N{:}C(S{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2)_2$, is obtained; it separates from acetic acid in sparkling, scarlet, spearhead shaped crystals, which melt at 148° and dissolve readily in chloroform.

o-*Nitrobenzyl phenyldithiocarbazinate*, $C_{14}H_{13}O_2N_3S_2$, is readily soluble in chloroform, ether, or benzene, less so in alcohol, and crystallises in pale yellow or white crystals melting at 142°. The alcoholic solution is coloured dark red by alkali hydroxide or carbonate. The *phenylhydrazone* of *di-o-nitrobenzyl dithiocarbonate* forms a felted mass of very slender, sparkling, golden needles melting at 94—95°.

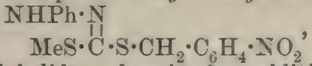
The *phenylhydrazone* of *methyl* p-*nitrobenzyl dithiocarbonate*,



$$NO_2\cdot C_6H_4\cdot CH_2\cdot S\cdot \overset{\overset{NHPh\cdot N}{\|}}{C}\cdot SMe,$$

prepared from *p*-nitrobenzyl chloride and phenyl methyl dithiocarbazinate, crystallises from alcohol in bundles of sparkling, orange-red needles or prisms melting at 84°, and is readily soluble in chloroform.

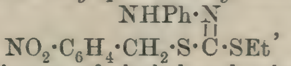
The *phenylhydrazone* of p-*nitrobenzyl methyl dithiocarbonate*,



$$MeS\cdot \overset{\overset{NHPh\cdot N}{\|}}{C}\cdot S\cdot CH_2\cdot C_6H_4\cdot NO_2,$$

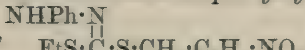
obtained from methyl iodide and *p*-nitrobenzyldithiocarbazinate, forms slender, lemon-yellow, silky needles melting at 89—90°. This form predominates in the mixture obtained by heating either of these two isomerides for an hour in a water-bath.

The *phenylhydrazone* of *ethyl* p-*nitrobenzyl dithiocarbonate*,



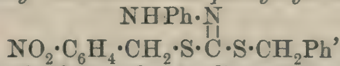
$$NO_2\cdot C_6H_4\cdot CH_2\cdot S\cdot \overset{\overset{NHPh\cdot N}{\|}}{C}\cdot SEt,$$

crystallises from a mixture of alcohol and ether in large, sparkling, scarlet prisms melting at 75°, and is readily soluble in benzene, chloroform, or ether and less so in alcohol. The isomeric *phenylhydrazone* of p-*nitrobenzyl ethyl dithiocarbonate*,



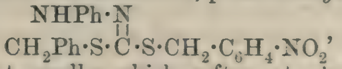
$EtS\cdot \overset{\overset{NHPh\cdot N}{\|}}{C}\cdot S\cdot CH_2\cdot C_6H_4\cdot NO_2$, separates from alcohol in silky, lemon-yellow needles which soften at about 40° and melt at 42°. In solubility, it differs but very slightly from its isomeride.

Benzyl p-*nitrobenzyl dithiocarbonate phenylhydrazone*,



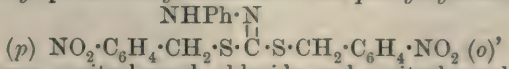
$$NO_2\cdot C_6H_4\cdot CH_2\cdot S\cdot \overset{\overset{NHPh\cdot N}{\|}}{C}\cdot S\cdot CH_2Ph,$$

forms shining, orange leaflets or flat needles melting at 98° and dissolves readily in chloroform. Its isomeride, p-*nitrobenzyl benzyl dithiocarbonate phenylhydrazone*,



$CH_2Ph\cdot S\cdot \overset{\overset{NHPh\cdot N}{\|}}{C}\cdot S\cdot CH_2\cdot C_6H_4\cdot NO_2$, forms large, glassy, orange-yellow, flat needles which soften at about 101° and melt at 103°. When heated for an hour at 110—120°, either of these isomerides yields approximately equal quantities of the two forms.

o-*Nitrobenzyl* p-*nitrobenzyl dithiocarbonate phenylhydrazone*,



$$(p)\ NO_2\cdot C_6H_4\cdot CH_2\cdot S\cdot \overset{\overset{NHPh\cdot N}{\|}}{C}\cdot S\cdot CH_2\cdot C_6H_4\cdot NO_2\ (o),$$

obtained from *p*-nitrobenzyl chloride and *o*-nitrobenzyl dithiocarbazinate, crystallises from a mixture of alcohol and ether in shining, many faced, garnet-red prisms melting at 81°, and dissolves readily in chloroform. The isomeric p-*nitrobenzyl* o-*nitrobenzyl dithiocarbonate*,

(*o*) $NO_2\cdot C_6H_4\cdot CH_2\cdot S\cdot \overset{NHPh\cdot N}{\overset{\|}{C}}\cdot S\cdot CH_2\cdot C_6H_4\cdot NO_2$ (*p*), separates from alcohol in long, orange to orange-red needles melting at 107°.

Unlike similar compounds with lower substituent radicles, the hydrazones described above are not capable of yielding salts with acids. With concentrated sulphuric acid they yield an emerald green colour, excepting those containing two benzyl residues, which give a bluish-green coloration; in both cases, the colour changes to yellow on heating. T. H. P.

Benzeneazopyrroles. By GIUSEPPE PLANCHER and E. SONCINI (*Atti Real. Accad. Lincei*, 1901, [v], **10**, i, 299—303).—Phenylcarbimide is found to react with benzeneazopyrrole and with benzenazo-2 : 4-dimethylpyrrole, both of which have the azo-group in the 2-position in the pyrrole nucleus, but no action takes place with either benzeneazo-2 : 5-dimethylpyrrole or benzeneazo-2-phenyl-5-methylpyrrole in which the azo-group occupies the 3-position. This would seem to indicate, not necessarily that the 3-benzeneazopyrroles are in the free state true azo-compounds and that the benzeneazopyrroles are really hydrazones, but that the 2-compounds are capable of acting in the tautomeric form in the presence of phenylcarbimide whilst the other derivatives are not. It is possible that the capability of reaction of the 2-compounds is due to the proximity of the imino-group of the phenylhydrazine residue to the basic nitrogen atom of the pyrrole nucleus.

Perfectly dry phenylcarbimide does not react with pyrrole, 2 : 5-dimethylpyrrole, 2 : 4-dimethylpyrrole, 5-phenyl-2-methylpyrrole, carbazole, succinimide, or iodole, either in the cold or on heating in the water-bath in presence of light petroleum.

Benzeneazopyrrole and phenylcarbimide yield a *compound*, $C_{17}H_{14}ON_4$, separating from light petroleum in yellowish-red needles melting at 108—110°.

Benzeneazo-2 : 4-dimethylpyrrole, $C_{12}H_{13}N_3$, separates from dilute alcohol in pale, garnet-red crystals melting at 118—119°. With phenylcarbimide it gives an unstable *compound*, $C_{19}H_{18}ON_4$, which melts at 70—71° and is readily resolved into its components.

Benzeneazo-2 : 5-dimethylpyrrole, already prepared by Fischer, who did not analyse it, and gave its melting point as 124°, has been prepared pure and analysed; its melting point is found to be 135°. It is a very stable, pale yellow compound, and does not react with phenylcarbimide.

Benzeneazo-2-methyl-5-phenylpyrrole was prepared and analysed. It is an orange-yellow compound which melts and decomposes at 120° with previous softening, and does not react with phenylcarbimide.

Tetrabromopyrrole, prepared but not analysed by Hepp, has been obtained by the authors, and has the composition C_4HNBr_4.

T. H. P.

Characterisation of Aminoazo-compounds. By RICHARD MÖHLAU and MAX HEINZE (*Ber.*, 1901, **34**, 881—888).—*Benzazophenylleucauramine*, $N_2Ph\cdot C_6H_4\cdot NH\cdot CH(C_6H_4\cdot NMe_2)_2$, prepared by the action of tetramethyldiaminobenzhydrol on *p*-aminoazobenzene, separates from a mixture of benzene and light petroleum in brownish-yellow prisms, melts at 156·5°, is slowly hydrolysed again by dilute acids, and gives acetyl-*p*-aminoazobenzene by the action of acetic anhydride and sodium acetate. Dimethylaminoazobenzene does not react with the benzhydrol.

Benzazo-α-naphthylleucauramine,

$$C_6H_5{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH{\cdot}CH(C_6H_4{\cdot}NMe_2)_2,$$

prepared from benzazo-*α*-naphthylamine and the benzhydrol, crystallises in yellowish-brown prisms, melts at 234—235°, and is decomposed like the preceding compound by dilute acids and by acetic anhydride.

p-*Tolueneazo*-p-*tolylleucauramine*,

$$C_6H_4Me{\cdot}N_2{\cdot}C_6H_3Me{\cdot}NH{\cdot}CH(C_6H_4{\cdot}NMe_2)_2\ [Me : NH : N_2 = 1 : 3 : 4],$$

prepared from *o*-azo-*p*-aminotoluene and the benzhydrol at temperatures below 40°, separates from a mixture of benzene and light petroleum in ruby-red needles and melts at 174·5°. When the action takes place between 40° and 80°, the *auramine*,

$$C_6H_4Me{\cdot}N_2{\cdot}C_6H_3Me{\cdot}N{:}C(C_6H_4{\cdot}NMe_2)_2,$$

is formed, and this is also produced by heating an alcoholic solution of the leucauramine; it crystallises from a mixture of benzene and light petroleum in orange-yellow flakes, melts at 190°, and is hydrolysed by mineral acids to *o*-azo-*p*-aminotoluene and tetramethyldiaminobenzophenone.

Benzazo-β-naphthylleucauramine,

$$C_6H_5{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH{\cdot}CH(C_6H_4{\cdot}NMe_2)_2,$$

prepared from benzazo-*β*-naphthylamine and the benzhydrol at temperatures below 40°, crystallises from hot acetone in scarlet needles and melts at 184°; by boiling an alcoholic solution of the leucauramine, a compound, $C_{33}H_{31}N_5$, is produced which melts at 74°, but is, perhaps, not the corresponding auramine, since tetramethyldiaminobenzophenone could not be found amongst the products of hydrolysis. T. M. L.

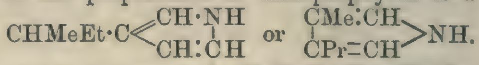
Formation of Acetone from Albumin. By Ferdinand Blumenthal and Carl Neuberg (*Chem. Centr.*, 1901, i, 788; from *Deut. med. Woch.*, **27**, 6—7).—Albuminous substances have been found to yield acetone when oxidised by means of iron salts. By digesting gelatin with hydrogen peroxide and a saturated solution of ferrous sulphate, acetone and an aldehyde are formed. The presence of the former is readily detected by Stock's method; to the distillate after treating with sodium hydroxide solution, hydroxylamine, and pyridine, ether is added and then bromine until the ethereal layer becomes yellow. On adding hydrogen peroxide, the yellow coloration becomes blue if acetone is present and by this means 1 part of acetone in 5000 of water can be detected. The aldehyde has not yet been examined. E. W. W.

Ichthulin from the Cod. By P. A. Levene (*Zeit. physiol. Chem.*, 1901, **32**, 281—284).—Ichthulin from the roe of the cod differs but very little in composition from the ichthulin obtained by Walter from carp roe (Abstr., 1891, 1389). When hydrolysed, however, it does not yield a sugar with reducing properties, and on treatment with alkalis gives *ichthulic acid* (C, 32·56; H, 6·0; N, 14·03; S, 0·146, and P, 10·34) which is very similar to vitellic acid (this vol., i, 300). Ichthulin from the cod resembles vitellin more than it does Walter's ichthulin. J. J. S.

Reduction Products and Constitution of Hæmin. By MARCELLUS NENCKI and J. ZALESKI (*Ber.*, 1901, **34**, 997—1010. Compare Abstr., 1896, ii, 335; 1900, i, 709).—*Mesoporphyrin*, $C_{16}H_{18}O_2N_2$, is obtained in the form of its *hydrochloride*, $C_{16}H_{18}O_2N_2,HCl$ when crude acetylhæmin is reduced with hydriodic acid of sp. gr. = 1·7 and glacial acetic acid and finally with phosphonium iodide, and the product crystallised several times fron dilute hydrochloric acid; the *base* forms a minutely crystalline, red coloured mass, and in its properties resembles hæmatoporphyrin. It is insoluble in water, and very sparingly soluble in alcohol or ether, but dissolves readily in alkalis, and does not melt at 340°. Its hydrochloride is decomposed by water, and its solutions, whether neutral, alkaline, or acid, appear to be identical spectroscopically with those of hæmatoporphyrin. When oxidised in hydrochloric acid solution with hydrogen peroxide, it yields a green compound,

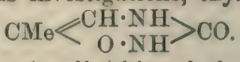
$$C_{16}H_{18}O_3N_2Cl_2,$$

probably chlorohæmatoporphyrin hydrochloride, $C_{16}O_{17}O_3N_2Cl,HCl$.

A bye-product obtained in the preparation of mesoporphyrin is a volatile oil *hæmopyrrole*,  $\mathrm{CHMeEt{\cdot}C}{<}\begin{matrix}\mathrm{CH{\cdot}NH}\\ \mathrm{CH{:}CH}\end{matrix}$ or $\begin{matrix}\mathrm{CMe{:}CH}\\ \mathrm{CPr{=}CH}\end{matrix}{>}\mathrm{NH}$. With mercuric chloride, it yields a *compound*, $(C_8H_{12}N)_2Hg,4HgCl_2$, sintering at 70°, and soluble in alcohol but insoluble in water. Its *picrate*, $C_8H_{13}N,C_6H_3O_7N_2$, crystallises from benzene in needles, melts at 108°, and decomposes at 125°.

When exposed to the air, the pyrrole base turns red, yielding urobilin, and when taken into the animal system it is also excreted in the form of urobilin. J. J. S.

Constitution of Thymine. By H. STEUDEL (*Zeit. physiol. Chem.*, 1901, **32**, 241—244. Compare Abstr., 1900, i, 467, and this vol., i, 108).—Details for the preparation of nitrothymine are given. When oxidised with barium permanganate, thymine yields a considerable amount of carbamide.

As a result of these and of the previous investigations, thymine is regarded as 5-*methyl*-2 : 6-*dioxypyrimidine*,  $\mathrm{CMe}{<}\begin{matrix}\mathrm{CH{\cdot}NH}\\ \mathrm{O{\cdot}NH}\end{matrix}{>}\mathrm{CO}$.

The compound, $C_4H_4O_2N_2$, described by Ascoli (this vol., i, 108) is probably 2 : 6-dioxypyrimidine. J. J. S.

Paranucleic Acid from Casein. I. By ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1901, **32**, 245—267).—An *iron* derivative of paranucleic acid is obtained when casein is digested with pepsin, the product evaporated, neutralised, and boiled with a 5 per cent. solution of iron alum. The average composition is C, 31·9; H, 4·43; N, 9·72; P, 2·55, and Fe, 21·87 per cent. It dissolves readily in moderately strong hydrochloric or in acetic acid, but is precipitated on dilution. It is also soluble in dilute sodium carbonate or hydroxide and also in aqueous ammonia, but is decomposed by concentrated sodium hydroxide, yielding ferric hydroxide and a solution which gives a precipitate when warmed with barium chloride solution. The liver of animals fed for 10 days on this iron compound becomes rich in iron; in some cases, it contains three times as much as was originally present.

Paranucleic acid is obtained when the iron compound is decomposed with sodium hydroxide and acidified with acetic acid; it is then converted into its *copper* derivative and this decomposed with hydrogen sulphide. The acid is readily soluble in water, but insoluble in alcohol or acetic acid. Its solutions are lævorotatory $[\alpha]_D$ $-46°$ (approx.), and give a precipitate when warmed with barium chloride solution. The acid is decomposed when boiled with sodium hydroxide of sp. gr. 1·34, yielding orthophosphoric acid. It gives precipitates with a hot solution of iron alum, mercuric chloride, copper acetate, lead acetate, tannin, phosphotungstic acid, saturated ammonium sulphate, or dilute egg-albumin. It also gives the biuret and xanthoprotein colour tests. J. J. S.

Coagulating Action of Papayotin on Solutions of Peptone. By D. Kuraéeff (*Chem. Centr.*, 1901, i, 788; from *Centr. med. Wiss.*, 1901, **39**, 145—147. Compare Okuneff and Lawroff, *Zeit. physiol. Chem.*, **26**, 513; Zawialoff, *Diss. Dorpat*, 1899).—When a solution of papayotin is added to a 10—18 per cent. solution of Witte's peptone which has been rendered alkaline by means of sodium carbonate and the mixture then digested at 40° for an hour, a flocculent precipitate is formed. By heating with alkalis, the precipitate becomes gelatinous and by the action of papayotin solutions on solutions containing more than 20 per cent. of peptone, gelatinous products are obtained. The papayotin acts as a ferment, for solutions which have been boiled are inactive. Solutions of caseoses and of the peptic products of muscle albumin are also attacked by papayotin. E. W. W.

Protoplasm and Enzymes. By Thomas Bokorny (*Pflüger's Archiv*, 1901, **85**, 257—270. Compare this vol., i, 177).—Chemical investigations on enzymes, so far as such have been possible, have shown that they are proteid or proteid-like in nature. Many, in fact, appear to be nucleo-proteid. Nucleo-proteid is also the main constituent of protoplasm. The similarity between protoplasm and enzymes is, indeed, very close. The action of acids, alkalis, antiseptics, and numerous other reagents, the influence of temperature and other agents, are all shown to be similar in both cases. W. D. H.

Catalase, a New Enzyme of General Occurrence, with Special Reference to the Tobacco Plant. By Oscar Loew (*U.S. Dept. Agr.*, *Rep.*, No. 68, 1901, pp. 47).—Catalase occurs in an insoluble (α-catalase) and in a soluble form (β-catalase), the former being probably a compound of β-catalase with a nucleo-proteid, whilst the latter is an albumose, and can be liberated from α-catalase by the action of very dilute alkali. The enzyme was found in every vegetable tested for it; leaves contain mainly α-catalase, whilst in seeds β-catalase predominates.

Both forms resist the effects of time longer than ordinary oxydases.

β-Catalase loses its power in aqueous solutions free from bacteria, and is killed by heating the solution at 71—75°; somewhat higher temperatures are required in very weak alkali solutions, and a lower temperature suffices in slightly acidified solutions. The temperature at which α-catalase is killed is about the same.

Mechanical motion greatly increases the action of catalase on hydrogen peroxide. Aqueous extracts of sweated tobacco (20 c.c.) mixed with hydrogen peroxide (10 c.c.) gave off 24 and 51 c.c. of oxygen respectively when left untouched and violently agitated.

Potassium nitrate (10 per cent.) has a very marked effect on depressing the activity of β-catalase, although the enzyme itself does not seem to be materially injured. Potassium salts retard the action more than sodium salts, and nitrates retard more than chlorides, sulphates, and carbonates. Even 3 per cent. solutions of anhydrous sodium carbonate attack β-catalase very slowly. Sodium fluoride (2 per cent.) and potassium oxalate (5 per cent.) cause no injury in twenty-four hours; and potassium thiocyanate and thiourea (5 per cent. solutions) seem to have no injurious effect on β-catalase, although they interfere with the action on hydrogen peroxide. Mercuric chloride is highly injurious.

Whilst highly dilute acids retard the action of α- and β-catalase, addition of 1 per cent. sodium carbonate to 10 c.c. of tobacco extract and 10 c.c. of hydrogen peroxide accelerated the evolution of oxygen. Acetic acid (0·1 per cent.) had no injurious effect in 1 hour, but gradually retarded the action at 35°. Sulphuric acid (2 per cent.) destroyed the catalytic power in 15 minutes; saturated baryta water kills β-catalase in two days, but α-catalase is more resisting. Absolute alcohol exerts no effect in twenty-four hours; even boiling absolute alcohol does not instantly kill the enzyme. Chloroform and ether in small amounts are without any marked effect. Phenol (1 per cent.) retards the action of the enzyme. Loss of activity occurs in presence of formaldehyde and of nitrous acid, indicating that labile amino-groups are concerned in the activity of the enzyme. Hydrogen cyanide readily kills β-catalase, whilst α-catalase shows considerable resistance. Hydrogen sulphide is injurious to α-catalase at the ordinary temperature, but the action is slow (compare Schönbein, *J. pr. Chem.*, 1863, 340); a good deal of sulphur is liberated. Hydroxylamine destroyed the soluble enzyme, but only retarded the action of the insoluble portion. Phenylhydrazine seems to form a still somewhat active compound with β-catalase; it reduces the activity of α-catalase. Alkaline silver solutions produced no effect on α-catalase; freshly precipitated silver oxide only had a moderate retarding effect on β-catalase.

Catalase is present in fungi in relatively very large amounts, and is produced by various bacteria (as, for instance, *Bacillus pyocyaneus*), the amount depending to some extent on the conditions of nutrition. It occurs in aqueous extracts of spleen, liver, brain, muscle, &c., but not in urine; also in infusoria, insects, worms, and molluscs.

The question whether catalase is an oxidising enzyme is discussed. α- and β-Catalase do not show a blue reaction with guaiacum, and do not produce the indophenol reaction; they have, however, the power of oxidising quinol.

As regards the physiological importance of catalase, it is suggested that its function may be to prevent any accumulation of hydrogen peroxide. In the case of yeast, it may be of importance for the action of Buchner's zymase.

The universal occurrence of catalase is sufficient proof that the statements of Clermont, Wurster, Bach, and E. Baumann, that hydrogen peroxide may occur in living cells, are incorrect. N. H. J. M.

Commercial Preparations of Diastase. By Georg Barth (*Zeit. angew. Chem.*, 1901, **14**, 368—371).—Using Lintner's method (Abstr., 1886, 386), the fermenting power of commercial preparations of diastase from eight different sources was estimated. The rapidity with which starch paste was clarified by the diastase was also tested. The details of the procedure in both these determinations are described in the paper. Five of the eight preparations exhibited little, if any, fermenting power; at the same time, they contained much starch, dextrin and reducing sugar and little nitrogen. Of the other three, Merck's diastase was a malt diastase, and had a fermenting power of 11·5 (on Lintner's standard); Witte's diastase was of animal origin and possessed a fermenting power of 27·4; Taka-diastase, obtained from the spores of certain moulds, exhibited a fermenting power of 8·63. K. J. P. O.

Properties of Galactase, a Digestive Ferment of Milk. By S. Moulton Babcock, H. L. Russell and Alfred Vivian (15th *Ann. Rep. Agr. Expt. Stat. Univ. Wisconsin*, for 1897—1898, 77—86. Compare Abstr. 1900, i, 712).—Galactase rapidly decomposes hydrogen peroxide. The optimum temperature of galactase, as indicated by digestive experiments with milk, seems to be between 37° and 42°. In experiments with milk, it was found that the enzyme is destroyed by exposure for 10 minutes to a temperature of 76° and its activity was reduced by heating for the same period at 70°. Experiments with gelatin showed that a reaction neutral or slightly alkaline to litmus is most favourable to the liquefaction of gelatin; decinormal acid and alkali solutions retarded the action.

As regards the effect of heat on the hydrogen peroxide test for galactase, it was found that decomposition always took place under conditions of neutrality or alkalinity when the temperature did not exceed 75° for 1 hour, and 80° for 10 minutes. The amounts of galactase were higher than in Storch's experiments with milk (40*th Rep. Copenhagen Expt. Stat.*).

Acid, especially hydrochloric, materially retards the activity of galactase, indicating that the enzyme belongs to the tryptic rather than to the peptic type. Mecuric chloride, formalin, phenol and its derivatives, and carbon disulphide destroy the enzyme.

The prolonged action of galactase on milk results in the formation of decomposition products of protein, ranging from albumoses to ammonia, with tyrosine, leucine, and other intermediate products.

N. H. J. M.

Action of Chemical Agents on Yeast and on the Enzymes obtained from it. By Thomas Bokorny (*Chem. Zeit.*, 1901, **25**, 365—366).—Various substances which completely kill the yeast cell do not destroy the fermentative functions of invertase; for example, 8 days' contact with absolute alcohol, 1 day with 5 per cent. formaldehyde, 1 day with chloroform, 16 days with 1 per cent. phenol. Twenty-four hours' contact with 0·2 per cent. acetic acid destroys the active properties of zymase, but even a 1 per cent. acid affects neither invertase nor maltase. Sixteen hours' contact with 0·5 per cent. sulphuric acid kills beer yeast, but not the mould forms of yeast ("Kahmhefe"). The enzymes are not so readily destroyed by sulphuric acid with the exception of zymase, which loses all its active properties after 24 hours' contact with 0·5 per cent., but not with 0·1 per cent. sulphuric acid. Alkalis (sodium hydroxide) also destroy the yeast protoplasm more readily than they do the enzymes.

Maltase is much more readily destroyed than invertase, in fact almost as readily as yeast protoplasm by most reagents. A 0·5 per cent. solution of oxalic acid, however, completely destroys the cell after 24 hours' contact but leaves the maltase intact. J. J. S.

Action of Invert Sugar on the Inversion of Sucrose by Sucrase. By VICTOR HENRI (*Compt. rend. Soc. Biol.*, 1901, **53**, 288—290, 290—292).—The rapidity of the inversion of sucrose by the invertase of yeast is lessened by the addition of invert sugar (dextrose and lævulose); it is accelerated if more sucrose is added during the process. Tables showing the quantitative relations are given. W. D. H.

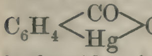
Philothion. By G. COSSETTINI (*Chem. Centr.*, 1901, i, 789; from *Boll. Chim. Farm.*, **40**, 75—76. Compare de Rey-Pailhade, Abstr., 1888, 1101; 1894, ii, 206).—When philothion is sterilised by filtering through a Chamberland filter, it loses its power of forming hydrogen sulphide from sulphur in cold solutions. E. W. W.

Dibenzylmethane- and Hydroxymethylenecamphor-phosphinic Acids. By AUGUST MICHAELIS and A. FLEMMING (*Ber.*, 1901, **34**, 1291—1300).—The substance, $C_{15}H_{17}O_3P$, obtained by Graebe (Abstr. 1875, 457) by the action of hydriodic acid and amorphous phosphorus on dibenzyl ketone, is dibenzylmethanephosphinic acid, $CH(C_7H_7)_2\cdot PO(OH)_2$. When this acid is strongly heated, it decomposes with formation of dibenzylmethane and a little toluene. *Tetranitro-* and *dinitro-dibenzylmethane* crystallise from chloroform in white needles and melt at 162—164° and 139° respectively. The *aniline* salt of dibenzylmethanephosphinic acid, $CH(C_7H_7)_2\cdot PO(OH)\cdot ONH_3Ph$, melts at 126°, and the *phenylhydrazine* salt at 148—149°; the *disilver* salt was also prepared. *Dibenzylmethaneoxychlorophosphine*,

$$CH(C_7H_7)_2\cdot POCl_2,$$

obtained by heating the acid (1 mol.) with phosphorus pentachloride (2 mols.) is a thick, colourless liquid which boils at 228° under 20 mm. pressure, has a sp. gr. 1·036 at 15°, and by the action of water is readily converted into the acid. Dibenzylmethanephosphinic *anhydride*, $CH(C_7H_7)_2\cdot PO_2$, obtained by heating equivalent quantities of the acid and the oxychlorophosphine in benzene solution, forms white, tabular crystals and melts at 151°. The *anilide*, $CH(C_7H_7)_2\cdot PO(NHPh)_2$, crystallises in white needles and melts at 196°. The *phenylhydrazide*, $CH(C_7H_7)_2\cdot PO(NH\cdot NHPh)_2$, melts at 164°. The *diethyl* ester boils at 240° under 20 mm. pressure; the *diphenyl* ester crystallises in hard, white prisms and melts at 120°, and the *ditolyl* ester melts at 131°. *Dibenzylmethanephosphinamic acid*, $CH(C_7H_7)_2\cdot PO(OH)\cdot NH_2$, obtained by the action of strong aqueous ammonia on the oxychlorophosphine, crystallises in lustrous, white leaflets, sinters at 230°, and melts at 244°; its *silver* salt is described.

Hydroxymethylenecamphorphosphinic acid, $C_{10}H_{14}O\colon CH\cdot PO(OH)_2$, was obtained by Bishop, Claisen, and Sinclair (Abstr., 1895, i, 63) as a bye-product in the preparation of hydroxymethylenecamphor, and was regarded by them as an acid phosphite; it crystallises with $\frac{1}{2}H_2O$, which is expelled at 110°; its *ammonium*, *silver*, and *lead* salts are described. The *aniline* salt, $C_{10}H_{14}O\colon CH\cdot PO(OH)\cdot ONH_3Ph$, melts at 195—196°. The *oxychlorophosphine*, $C_{10}H_{14}O\colon CH\cdot POCl_2$, obtained by heating the acid (1 mol.) with phosphorus pentachloride (2 mols.), boils in a vacuum at 175—185°, and forms white, tabular crystals melting at 51°; by the action of water, it is readily converted into the acid. The *anilide*, $C_{10}H_{14}O\colon CH\cdot PO(NHPh)_2$, crystallises in slender, yellow needles and melts at 227—228°; the p-*toluidide* and the p-*diphenetidide* melt at 210° and 137° respectively. The *diethyl* ester boils at 195—205° under 20 mm. pressure, and is decomposed by water. E. G.

Direct Introduction of Mercury into Aromatic Compounds. By OTTO DIMROTH and, in part, RICHARD METZGER and HERMANN ILZHÖFER (*Chem. Centr.*, 1901, i, 449—455; from *Habilschr.*, Tübingen, 1900).—Many of the results contained in this dissertation have been published already (Abstr., 1899, i, 54, 428), and the methods employed are those described before. The following observations appear to be new. The ease with which aromatic compounds form arylmercuric salts is on a level with the ease with which they can be nitrated or sulphonated; phenols and amines react readily, hydrocarbons and benzoic acid less readily, and nitrobenzene not at all. The mercury enters the usual position in the ring; in the case of benzoic acid, however, it enters the ortho-, and not the meta-position, but the reaction is otherwise abnormal, for a cyclic anhydride,  $C_6H_4<\genfrac{}{}{0pt}{}{CO}{Hg}>O$, is formed. A solution of stannous chloride in alkali hydroxides is found to reduce arylmercuric chlorides, HgRCl, to mercury and mercury aryls, HgR_2. Alkalis do not decompose arylmercuric salts. Ammonium sulphide converts them into white sulphides; it does not attack mercury aryls; it instantly decomposes compounds in which the mercury is joined to nitrogen, such as mercurianiline, $Hg(NHPh)_2$, black mercuric sulphide separating. *o*-Hydroxyphenylmercuric chloride unites with benzenediazonium chloride to form an azo-dye; under these circumstances, the para-isomeride is decomposed into mercuric chloride and hydroxyazobenzene, whilst the behaviour of hydroxyphenylenedimercuric chloride is of an intermediate character, some mercuric chloride being eliminated, and benzeneazo-*o*-hydroxyphenylmercuric chloride formed. Benzenesulphonic acid forms a meta-mercury derivative, but this could not be obtained quite pure. Naphthalene also forms a mercury derivative.

The following substances appear to be described for the first time (the numbers given are melting points). From phenol: o-*Mercuridiphenol*, $Hg(C_6H_4\cdot OH)_2$, from *o*-hydroxyphenylmercuric chloride and sodium thiosulphate (compare Pesci, Abstr., 1899, i, 816). *Anisylmercuric iodides*, o, 168°, p, 227°. o-*Phenetylmercuric iodide*, 111°. p-*Hydroxyphenylmercuric oxide* decomposes at 180°. *Hydroxyphenylenedimercuric diacetate*, decomposes at 264—265°; invariably the product when mercuric acetate acts on phenol. *Benzeneazo-o-hydroxyphenylmecuric chloride*, red, 147°; crystallised with $1CMeO\cdot OH$, yellowish-brown, 126—128°; with $1\frac{1}{2}H_2O$, yellow, about 125°; the last compound loses its water in a desiccator, forming a hygroscopic powder that takes up $1H_2O$ in the air, and at a higher temperature forms the substance melting at 147°. *Benzeneazo-*p-*hydroxyphenylmercuric chloride*, red, 130—131°; *acetate*, yellow. *Benzeneazo-*o-*hydroxyphenylmercuric acetate*, yellow, 197—198°. *Benzeneazohydroxyphenylenedimercuric dichloride*, about 165—170° (crystallised with $1CMeO\cdot OH$, brownish-red), is formed in small amount along with the preceding compound.

From *p*-cresol: 4-*Hydroxy*-1-*methylphenylene*-3:5-*dimercuric acetate*, decomposes at about 200°. 4-*Hydroxy*-1-*methylphenyl*-3-*mercuric chloride*, 166°; solid again at 183°; *benzoate*, 241—242°; 3-*iodo*-4-*hydroxy*-1-*methylbenzene* (o-*iodocresol*), 37°, boils at 117° under a pressure of 12 mm. *Hydroxymethylphenylmercuric oxide* decomposes in light. *Benzeneazohydroxymethylphenylmercuric acetate*, red, 269°; *chloride*, yellowish-brown, decomposes about 249°; *benzeneazohydroxymethylbenzene* (*benzeneazo*-p-*cresol*), 108—109°.

From phenetole (compare Michaelis, Abstr., 1894, i, 191): p-*Phenetylmercuric acetate*, 234°. No *o*-isomeride discovered.

From aniline: p-*Aminophenylmercuric acetate*, 166—167° (compare Piccini and Ruspagiari, Abstr., 1893, i, 322), *acetyl* derivative, 220—221°; *chloride*. A second *product*, 158—160°, probably the isomeric *o*-acetate, was also obtained; *acetyl* derivative, 158—160°.

From dimethylaniline (compare Pesci, Abstr., 1894, i, 248): p-*Dimethylaminophenylmercuric acetate*, 165°; *chloride*, 225°.

From benzenesulphonic acid (see preceding page): By treating the product with bromine, m-*bromobenzenesulphonic acid* and some *dibromobenzenesulphonic acid* are obtained; the *sodium* salt of the former crystallises with $1H_2O$.

From benzoic acid: *Mercuric benzoate*, 165°, when heated yields the amorphous *anhydride* of o-*carboxyphenylmercuric hydroxide* (o-*hydroxymercuric benzoic anhydride*; see preceding page).

From naphthalene: α-*Naphthylmercuric acetate*, 245—250°; *chloride*; *naphthylenedimercuric dichloride*. C. F. B.

Organic Magnesium Compounds of the Benzene Series. By Tissier and Guignard (*Compt. rend.*, 1901, **132**, 1182—1184).—The haloid derivatives of benzene and its homologues react readily with magnesium in presence of ether, forming crystalline compounds of the type MgPhBr and $C_7H_7\cdot MgBr$, analogous to those obtained with the paraffins. These compounds react energetically with acid chlorides and anhydrides, esters, and primary and secondary aldehydes, yielding products which will be described later.

Magnesium phenyl bromide with methyl benzoate yields triphenylcarbinol in almost theoretical quantity; with acetone, it yields dimethylphenylcarbinol, and with acetyl chloride, diphenylethylene, $CPh_2{:}CH_2$.
C. H. B.

Organic Chemistry.

Composition of Texas Petroleum. By Charles F. Mabery (*J. Amer. Chem. Soc.*, 1901, **23**, 264—267. Compare Abstr., 1900, i, 577).—A specimen of oil from the Lucas well in Jefferson Co. possessed a strong odour of hydrogen sulphide, had a sp. gr. 0·920 at 20°, and contained 2·16 per cent. of sulphur, and more than 1 per cent. of nitrogen. By fractional distillation under 14 mm. pressure and subsequent treatment with fuming sulphuric acid, the following hydrocarbons were isolated: fraction 130—135°, $C_{12}H_{22}$, sp. gr. 0·8553 at 20°; fraction 155—160°, $C_{14}H_{26}$, sp. gr. 0·8746, molecular refraction 62·36; fraction 190—195°, $C_{16}H_{30}$, sp. gr. 0·8915, molecular refraction 71·64; the residue left above 300° showed a sp. gr. 14° Beaumé.

The author suggests that these hydrocarbons possess the structure of a dihexahydrodiphenyl and its homologues. E. G.

Hexyl Bromide. By Antoine Mouneyrat (*Bull. Soc. Chim.*, 1901, [iii], **25**, 543).—A reply to Bodroux (this vol., i, 306). N. L.

Oxidation of Primary Alcohols by Contact-action. By J. Auguste Trillat (*Compt. rend.*, 1901, **132**, 1227—1229).—On passing a mixture of air and the vapour of one of the primary alcohols of the fatty series over a platinum spiral heated to redness, the corresponding aldehyde is always formed, and represents from 1·8 to 1·5 per cent. of the alcohol used. The presence of water vapour does not modify the oxidation. Methyl and ethyl alcohol also yield methylal and acetal respectively. The latter action is reversible, as on passing the vapour of either of these acetals over a spiral, the aldehyde and alcohol are regenerated, a decomposition accompanied by a sufficient development of heat to render the spiral incandescent. Even in the absence of air, acetaldehyde is formed from ethyl alcohol. In the presence of platinum black or porous substances, the alcohols are oxidised to the corresponding acids. Besides the alcohols mentioned, the author has experimented with propyl, *iso*propyl, normal butyl, *iso*amyl, normal heptyl, and primary octyl alcohols. K. J. P. O.

Alcohols and Calcium Carbide. By Pierre Lefebvre (*Compt. rend.*, 1901, **132**, 1221—1223. Compare Abstr., 1900, i, 323).—On passing amyl, *iso*butyl, ethyl and methyl alcohols over calcium carbide heated at about 500° in tubes of iron or of Jena glass, a mixture of gases is obtained, which, in all four cases, consists chiefly (from 60—70 per cent.) of hydrogen. When a glass tube is used, amyl alcohol yields, besides hydrogen, acetylene 2·5, ethylene 4·9, carbon monoxide 8·6, carbon dioxide 2·2, ethylene hydrocarbons 8·6, and ethane 8·0 per cent. In an iron tube, the ethane increases at the expense of the ethylene hydrocarbons. When the calcium carbide is replaced by porcelain, only a trace of acetylene is formed, and the carbon monoxide increases to 12·4 and the ethylene hydrocarbons to 14·3 per cent., whilst 4·2 per cent. of ethane is produced. Analyses of the bromine derivatives of the ethylene hydrocarbons show that they consist of propylene ($\frac{1}{2}$ to $\frac{3}{4}$), a trace of butylene, and the remainder β-methyl-β-butylene; no trimethylene is present.

From *iso*butyl alcohol were produced, acetylene 3·8, ethylene 4·8, carbon monoxide 6·8, *iso*butylene 7·8, ethane 13·4, and carbon dioxide 1·9 per cent. From ethyl alcohol were obtained, acetylene 3·6, ethylene 9·1, carbon monoxide 4·5, ethylene hydrocarbons 0·31, ethane 9·6, and carbon dioxide 4·4 per cent.; from methyl alcohol, acetylene 1·4, ethylene 4·2, carbon monoxide 8·3, ethylene hydrocarbons 2·5, ethane 13·8, and carbon dioxide 1·3 per cent. The liquid products of the reaction consisted in all cases (with the exception of methyl alcohol) of the aldehyde corresponding with the alcohol, and amounted to about 10 per cent. of the alcohol used. K. J. P. O.

Molecular Compound of Methyl Iodide with Methyl Alcohol. By JEAN MEUNIER (*Bull. Soc. Chim.*, 1901, [iii], **25**, 572—573).—If the product of the interaction of methyl alcohol, iodine, and phosphorus produced in the preparation of methyl iodide is distilled without removal of the methyl alcohol by washing with water, the *compound* $MeI,\frac{1}{3}CH_4O$ is obtained. This is a colourless, highly refractive liquid which boils at 37·9°, and has a sp. gr. 2·0807 at 15°; it is readily decomposed by water. N. L.

Active Amyl Derivatives. By PHILIPPE A. GUYE (*Bull. Soc. Chim.*, 1901, [iii], **25**, 544—551. Compare Abstr., 1895, i, 202, 317, and ii, 472; 1897, ii, 238; 1898, ii, 469; 1899, ii, 718; 1900, ii, 253).—The amyl derivatives, the optical properties of which have been previously studied by the author, were prepared from Claudon's amyl alcohol, having a rotatory power $[\alpha]_D$ −4°·52 at 20°, whereas pure active amyl alcohol, according to Marckwald and Mackenzie (this vol., i, 248), has $[\alpha]_D$ −5°·90 at 20°. A number of observations bearing on the subject are now recalled from the author's researches, and it is shown that the *relative* values previously found for the rotatory powers of amyl derivatives are probably correct, and may be converted into the approximate *absolute* values by multiplying by the factor 5·90/4·52 or 1·305. Tables of the original and corrected values for a number of compounds are given in the paper. N. L.

Action of Aluminium Chloride on Aliphatic Alcohols. By GUSTAVE PERRIER and ISIDORE POUGET (*Bull. Soc. Chim.*, 1901, [iii], **25**, 551—556).—The action of aluminium chloride on aliphatic alcohols in the cold results in the formation of additive compounds, whilst if the alcohol is heated with a large excess of aluminium chloride, substitution derivatives are formed. The following *compounds*, all of which are white, crystalline substances decomposed by water, have been prepared from methyl, ethyl, and *iso*butyl alcohols: $Al_2Cl_6,10MeOH$; $Al_2Cl_4(OMe)_2$; $Al_2Cl_6,8EtOH$; $Al_2Cl_3(OEt)_3$; $Al_2Cl_6,4C_4H_9{\cdot}OH$; $Al_2Cl_4(OC_4H_9)_2$. Similar compounds are also formed from *n* propyl and *iso*amyl alcohols. N. L.

Condensation of the true Acetylene Hydrocarbons with Formaldehyde. Synthesis of Primary Alcohols of the Acetylene Series. By CHARLES MOUREU and H. DESMOTS (*Compt. rend.*, 1901, **132**, 1223—1226).—On treating the sodium derivatives of acetylene hydrocarbons suspended in absolute ether with excess of trioxymethylene, a reaction immediately takes place. After removing the sodium with dilute sulphuric acid and evaporating the ether, the alcohol formed is fractionated under reduced pressure; the yield is about 30 per cent. From œnanthylidene [heptinene] *amylpropargyl* [*β-octinyl*] *alcohol*, $CH_2Me\cdot[CH_2]_3\cdot C\vdots C\cdot CH_2\cdot OH$, is obtained as a colourless oil boiling at 98° under 13 mm. pressure, and having a sp. gr. 0·8933 at 0°. The *acetate* boils at 113—114° under 16 mm. pressure. In the same reaction is also formed a *compound*, $C_{16}H_{26}O$, which is possibly a condensation product of 2 mols. of β-octinyl alcohol. It boils at 178° under 16 mm. pressure, has the sp. gr. 0·907 at 0° and 0·892 at 19°, and gives n_D 1·474 at 19°.

Phenylacetylene yields *phenylpropargyl alcohol*, $CPh\vdots C\cdot CH_2\cdot OH$, which is a colourless oil boiling at 139° under 16 mm. pressure and having a sp. gr. 1·0811 at 0°. The *acetate* boils at 146° under 16 mm. pressure. Neither of these alcohols solidifies at $-23°$; each forms a crystalline compound with aqueous solutions of mercuric chloride, reduces ammoniacal silver nitrate, and is not affected by boiling with potassium hydroxide solution. As the typical hydrogen atom of the acetylene hydrocarbons has disappeared, compounds with silver, &c., are not obtainable. K. J. P. O.

Chloro- and Bromo-methyl Alcohols. By FRANZ M. LITTERSCHEID (*Annalen*, 1901, **316**, 157—195).—A commercial "chloromethyl alcohol" was found to consist principally of chloromethyl ether mixed with small quantities of *s*-dichloromethyl ether and dichlorotrioxytetramethylene, $O(CH_2\cdot O\cdot CH_2Cl)_2$, together with traces of methylal and varying amounts of hydrogen chloride. Chloromethyl ether was identified by its boiling point and the analysis of the double salts of its compounds with trimethylamine and pyridine, the following *compounds* being described: $(OMe\cdot CH_2\cdot NMe_3Cl)_2PtCl_4$,
$(OMe\cdot CH_2\cdot NMe_3Cl)AuCl_3$,
$(OMe\cdot CH_2\cdot C_5NH_5Cl)_2PtCl_4$, and $(OMe\cdot CH_2\cdot C_5NH_5Cl)AuCl_3$ (compare Hemmelmayr, Abstr., 1892, 504).

s-Dichloromethyl ether was identified in a similar manner, the following *double* salts being described: $O(CH_2\cdot NMe_3Cl)_2,AuCl_3$ and $[O(CH_2\cdot NMe_3Cl)_2]_2,PtCl_4,H_2O$, the latter melting at 237°.

Dichlorotrioxytetramethylene yields the amorphous *double* salt, $O(CH_2\cdot O\cdot CH_2\cdot NMe_3Cl)_2PtCl_4,H_2O$, and the corresponding aurichloride crystallising with $1H_2O$.

When hydrogen chloride reacts with gaseous formaldehyde, the chief products are *s*-dichloromethyl ether and dichlorotrioxytetramethylene (compare Grassi and Maselli, Abstr., 1899, i, 409).

The chief product of the action of hydrogen bromide on trioxymethylene, or on an aqueous solution of pure formaldehyde, is *s*-dibromomethyl ether; no evidence could be obtained that bromomethyl alcohol is formed under these conditions (compare Henry, *Bull. Acad. Roy. Belg.*, 1893, [iii], **26**, 615).

With trimethylamine, the bromo-ether yields the *bromide*, $O(CH_2\cdot NMe_3Br)_2,H_2O$; this salt loses water when dried at 100°, and melts at 205°. G. T. M

Compounds of Methyl Sulphide with Haloids of Metals. By FRANCIS C. PHILLIPS (*J. Amer. Chem. Soc.*, 1901, **23**, 250—258).—When methyl sulphide is added to a solution of palladium dichloride, the *compound* $PdCl_2,2Me_2S$ is produced as a voluminous, yellow, microcrystalline precipitate, which dissolves readily in boiling water and separates in orange needles on cooling. In solution, it is reduced by carbon monoxide, or more slowly by hydrogen, whilst in the solid state it is reduced by hydrogen in the cold with liberation of methyl sulphide and hydrogen chloride. Its solubility in water is 0·15 per cent. at 26·1°; it dissolves in most organic solvents, melts at 124°, and, when heated more strongly, decomposes with formation of methyl sulphide, methyl chloride, and palladium sulphide.

Methyl sulphide combines with mercuric chloride to form a white, crystalline compound, $3HgCl_2,2Me_2S$, which is slightly soluble in water and more so in alcohol; when heated rapidly, it melts at about 150—151° with evolution of methyl sulphide, but if heated more slowly, it decomposes and melts at a much higher temperature. This substance was first obtained by Loir (*Annalen*, 1853, **87**, 369), who assigned to it the formula $HgCl_2,Me_2S$.

If methyl sulphide is added to a concentrated solution of cupric chloride, a white, crystalline *substance*, $CuCl,Me_2S$, slowly separates, which, when heated in nitrogen, evolves methyl sulphide, and leaves finally a residue of copper sulphide and copper; it is almost insoluble in water and the usual organic solvents.

Methyl sulphide reacts with a solution of auric chloride with formation of a *compound*, $AuCl,Me_2S$, which separates as a white, flocculent precipitate, but if left in the dark with a slight excess of methyl sulphide forms crystalline needles; it is rapidly decomposed by sunlight, yielding gold, methyl sulphide, and hydrogen chloride; when it is heated in nitrogen, methyl sulphide is evolved and metallic gold is left as a residue.

E. G.

Constitutional Formulæ of Acids. By DANIEL VORLÄNDER (*Ber.*, 1901, **34**, 1632—1637).—It is pointed out that all pronounced organic (and most inorganic) acids possess the atomic grouping $\underset{1}{H}\cdot\underset{2}{E}\cdot\underset{3}{E}\colon\underset{4}{E}$ (for example, $\underset{1}{H}\cdot\underset{2}{O}\cdot\underset{3}{C}\colon\underset{4}{O}$). The mobility of the hydrogen atom depends firstly on the non-metal, 2, and secondly on the unsaturated character of the linking between the non-metals, 3 and 4 (called by the author the "reactive group").

The hydrogen is far less movable in the absence of an unsaturated linking so placed, as in the types $\underset{1}{H}\cdot\underset{2}{E}\colon\underset{3}{E}$ and $\underset{1}{H}\cdot\underset{2}{E}\cdot\underset{3}{E}\cdot\underset{4}{E}\colon\underset{5}{E}$. As examples, the properties of the hydrogen atom in the aldehyde group $H\cdot C\colon O$, and in the acid group $H\cdot O\cdot C\colon O$, are compared; and also in the groupings $H\cdot O\cdot C\cdot(C\colon C)_3$ in triphenylcarbinol, and $H\cdot O\cdot C\colon C$ in phenol. The acid character of the hydroxymethylene derivatives similarly finds its explanation in the atomic grouping $H\cdot O\cdot C\colon C$. This grouping is absent in hypochlorous acid, $H\cdot O\cdot Cl$, which is very feebly acidic, despite the presence of the non-metal chlorine, which gives to hydrochloric acid such powerful acid properties.

K. J. P. O.

Ethyl Nitroacetate. By A. WAHL (*Compt. rend.*, 1901, **132**, 1050—1053. Compare this vol., i, 4).—Ethyl nitromalonate, conveniently prepared by adding ethyl malonate to fuming nitric acid at 20—30° (compare Franchimont, Abstr., 1889, 1143), is separated from the product of reaction in the form of its *potassium* derivative, $C_7H_{10}O_6NK$, a compound separating from alcohol in lemon-yellow crystals; the *sodium* derivative crystallises in pale yellow needles. These substances are both readily soluble in water, and when heated melt and deflagrate with extreme violence; they regenerate the ester on treatment with dilute acids.

Ethyl nitromalonate is a colourless liquid boiling unchanged at 127° under 10 mm. pressure; it has the sp. gr. 1·1988 at 20°, and 1·220 at 0°, and is slightly soluble in water, yielding a yellow solution. When heated with water under pressure at 160°, it is completely decomposed, hydrocyanic and oxalic acids being identified among the degradation products. On slowly adding an aqueous solution of potassium hydroxide to a boiling solution of the potassium derivative of ethyl nitromalonate, the latter is decomposed, and the product, after acidifying, gives a yellow oil; this on fractionation yields a colourless liquid boiling at 90—95° under 10 mm. pressure, which is identical with the ethyl nitroacetate obtained from ethyl dimethylacrylate. G. T. M.

Action of Acid Chlorides on Ethers in the presence of Zinc. By PAUL FREUNDLER (*Compt. rend.*, 1901, **132**, 1226—1227. Compare this vol., i, 357).—The author draws attention to the fact that Descudé's results (*loc. cit.*) have been partly anticipated by Freund (*Annalen*, 1861, **118**, 33), who found that by the action of zinc on a mixture of butyryl chloride and ethyl ether, ethyl butyrate, ethyl chloride, zinc chloride, and dipropyl diketone were formed. Using zinc chloride instead of zinc, Descudé obtained an ester and alkyl chloride. The author obtained the same result when employing a zinc-copper couple. K. J. P. O.

Waxes. By MAURITS GRESHOFF and J. SACK (*Rec. Trav. Chim.*, 1901, **20**, 65—78).—A wax, $C_{37}H_{74}O_2$ (*cera musae*), found on the leaves of the wild Javan banana-tree or "pisang," may be purified by melting in boiling water, and after solidification forms hard, white, vitreous masses having a crystalline, powdery fracture; it melts at 79—81°, has a sp. gr. 0·963 to 0·970 at 15°, and is sparingly soluble in all solvents. At 15°, light petroleum dissolves 0·4, acetone 0·5, ether 0·7, chloroform 1·7, and carbon disulphide 1·8 parts per 100. On hydrolysis with alcoholic potash, it yields a crystalline *acid*, $C_{24}H_{48}O_2$, melting at 71°, and an *alcohol*, $C_{13}H_{28}O$, melting at 78°; the acid is perhaps identical with the fatty acid of the same composition melting at 72°, which is formed by the hydrolysis of Carnauba wax.

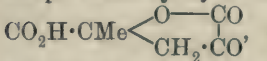
Another wax (*cera fici*) is obtained from the sap exuding from incisions in the cortex of the wild fig tree or "gondang" (*Ficus ceriflua*); it is chocolate coloured externally, and cream coloured within, is not friable, and melts at about 60° to an extraordinarily viscous mass which only slowly solidifies, and is then nearly white. The molten wax has a sp. gr. 1·015 at 15°; by successive crystallisations from alcohol, it yields principally a crystalline *compound*, $C_{30}H_{52}O_2$, melting at 61°. On hydrolysing this, an alcohol, *ficocerylic alcohol*, $C_{17}H_{28}O$, which crystallises from alcohol and melts at 198°, is obtained, along with an acid, *ficoceroic acid*, $C_{13}H_{26}O_2$, which melts at 57°. Small quantities of ficocerylic alcohol are present in the free state in the original wax, but are removed when the latter is crystallised from alcohol.

When the wax of the gondang is subjected to dry distillation, it yields acetic and propionic acids, a *hydrocarbon*, $C_{14}H_{26}$, which boils at 220° and has a sp. gr. 0·845 at 15°, and two crystalline *acids*, which can be separated by means of alcohol; *one* of these, $C_{44}H_{88}O$, melts at 51° and the *other*, $C_{12}H_{24}O_2$, at 54°.

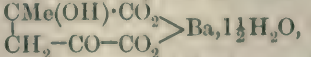
The dry distillation of the wax of pisang yields a liquid *hydrocarbon*, $C_{16}H_{34}$, boiling at about 280°, and an *acid*, $C_{27}H_{54}O_2$, which crystallises from alcohol and melts at 58°.

Bees' wax when distilled yields an oil which boils evenly between 180° and 250°, the fractions of highest boiling point (220—250°) having the composition of a *hydrocarbon*, $C_{15}H_{30}$; a crystalline solid is also formed, which on hydrolysis yields an *acid*, $C_7H_{14}O_2$ (?), melting at 63°, and a non-saponifiable residue which is apparently a hydrocarbon of the series C_nH_{2n}, and melts at 56°. W. A. D.

Action of Hydrochloric Acid on Pyruvic Acid. By A. W. K. de Jong (*Rec. Trav. Chim.*, 1901, 20, 81—101).—The *sodium sulphite* compound, $CH_3\cdot CO\cdot CO_2Na,NaHSO_3,H_2O$, of sodium pyruvate crystallises from water on slow evaporation in orthorhombic prisms [$a:b:c = 0·7485:1:0·5258$], and when decomposed at the ordinary temperature by hydrochloric acid of sp. gr. 1·14 yields the *γ-lactone*,

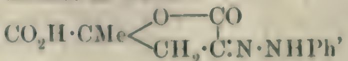


$CO_2H\cdot CMe<\begin{array}{l}O\text{——}CO\\CH_2\cdot CO\end{array}$, of *α-keto-γ-hydroxybutane-αγ-dicarboxylic acid*; this can also be obtained by leaving pyruvic acid in contact with hydrochloric acid of sp. gr. 1·14 for several months, or more rapidly (after about 8 days) by passing dry hydrogen chloride through pyruvic acid until crystals begin to form. It is slowly formed by the spontaneous condensation of pyruvic acid (compare Wolff, Abstr., 1899, i, 483), and is usually present in commercial samples of the latter; when pure, it crystallises in needles, melts at 115—116° and is hygroscopic. Its formula was confirmed by a molecular weight determination by the cryoscopic method in glacial acetic acid solution. The *barium* salt, with $1\frac{1}{2}H_2O$, of the lactone is obtained by neutralising it with barium carbonate, and adding alcohol. It forms slender needles, is easily soluble in water and, when boiled with it, is transformed into the *barium* salt, $[CO_2H\cdot CMe(OH)\cdot CH_2\cdot CO\cdot CO_2]_2Ba$, of α-keto-γ-hydroxybutane-αγ-dicarboxylic acid; this forms a crust of needles, is less soluble in water than the salt of the lactone, and when decomposed by dilute sulphuric acid yields, not the corresponding acid, but its lactone. The normal *barium* salt,



$\begin{array}{l}CMe(OH)\cdot CO_2\\CH_2-CO-CO_2\end{array}>Ba,1\frac{1}{2}H_2O$, formed by neutralising a warm solution of the lactone with barium carbonate, is amorphous and easily soluble in water.

The *phenylhydrazone*,



$CO_2H\cdot CMe<\begin{array}{l}O\text{——}CO\\CH_2\cdot C:N\cdot NHPh\end{array}$, of the lactone forms sheaves of slender, yellow needles, melts at 191—192°, and usually crystallises with $2H_2O$, although from concentrated solutions it is obtained anhydrous. Tests are given which distinguish this phenylhydrazone from the phenylhydrazone of pyruvic acid which melts at 185° as stated by Japp and Klingemann (Trans., 1887, **51**, 533) and not at 192° as stated by E. Fischer (Abstr., 1884, 1150); it is probable that Fischer's compound was the phenylhydrazone of the new lactone. The same phenylhydrazone is formed on adding phenylhydrazine hydrochloride to a solution of the barium salt of the lactone, but the two barium salts of the acid yield instead the *phenylhydrazone*, $CO_2H\cdot CMe(OH)\cdot CH_2\cdot C(CO_2H):N\cdot NHPh$, of this acid; it crystallises in needles with $2H_2O$ and melts at 154—155°.

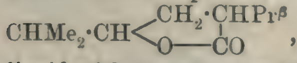
α-Keto-γ-hydroxybutane-αγ-dicarboxylic acid, which can be considered as formed by the aldol condensation of pyruvic acid, when heated with hydrochloric acid yields pyrotartaric acid; with sodium hydroxide, it forms methyldihydrotrimesic acid. W. A. D.

Action of Sodium on the Esters of Organic Acids. By SERGIUS N. REFORMATSKY (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 235—239).—The author discusses the mechanism of the formation of ethyl acetoacetate by the action of sodium on ethyl acetate, as given by Claisen, with whose views the results given in the following two papers agree. T. H. P.

Synthesis of α-Methyl-β-ethylhydracrylic Acid. By A. ASTACHOFF and SERGIUS N. REFORMATSKY (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 239—241).—The ethyl ester of this acid, already described by Hantzsch and Wohlbrück (Abstr., 1887, 717) is obtained by the action of zinc on a mixture of ethyl α-bromopropionate and propaldehyde and decomposition of the resulting product with water.

T. H. P.

Synthesis and Properties of α-*iso*Propyl-β-*iso*butylhydracrylic Acid. By D. PROTOPOPOFF and SERGIUS N. REFORMATSKY (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 242—246).—The constitution of α-*iso*propyl-β-*iso*butylhydracrylic acid, $C_{10}H_{20}O_3$, obtained by Wohlbrück (Abstr., 1887, 1099) by the action of sodium on ethyl *iso*valerate, is confirmed by its formation when zinc, ethyl bromo*iso*valerate, and *iso*valeraldehyde interact. The *ethyl* ester, $C_{12}H_{24}O_3$, forms a thick oil distilling at 188—190° under 140—150 mm. pressure. The *sodium* and *basic barium*, $(C_{10}H_{19}O_3)_2Ba,Ba(OH)_2$, salts were analysed. The mean value of the electrical conductivity constant is $K=0{\cdot}00199$, the mean number for secondary β-hydroxy-acids being 0·0018. By distillation with 10 per cent. sulphuric acid, the acid yields: (1) a *lactone*,



$CHMe_2\cdot CH<\begin{matrix}CH_2\cdot CHPr^{\beta}\\ O\text{—}CO\end{matrix}$, which is a neutral, colourless, viscous liquid with a smell resembling that of camphor; it does not decolorise bromine, is slightly soluble in water, and boils at 241—243°; (2) a small quantity of colourless crystals melting at 68—69·5° which have an acid reaction and decolorise bromine and represent probably an αβ-unsaturated acid, since the original hydroxy-acid has a hydrogen atom in the α-position. T. H. P.

Urano-oxalic Acid. By VOLKMAR KOHLSCHÜTTER and H. ROSSI (*Ber.*, 1901, **34**, 1472—1479).—When oxalic acid is added to a solution of a uranyl salt reduced with copper or with hyposulphurous acid, a green, crystalline precipitate of insoluble uranous oxalate, $U(C_2O_4)_2,6H_2O$ (Seekamp, *Annalen*, 1862, **122**, 115), is produced; the precipitate is formed quantitatively and can be used for estimating uranium or for recovering uranium from complex residues; unlike other uranous salts, it is not readily oxidised; it is insoluble in water and in dilute acids, but dissolves in concentrated hydrochloric acid; alkalis convert it into uranous hydroxide. With ammonium and potassium oxalates, it gives dichroic solutions of urano-oxalates which are green in thick layers and red in thin layers; *potassium urano-oxalate*, $U(\cdot O\cdot CO\cdot CO_2K)_4$, forms rhombic crystals, which are only slightly coloured, but gives a dichroic solution; it is very stable when compared with other uranous salts; *barium urano-oxalate*, $U(C_2O_4)_4Ba_2,9H_2O$, is a violet, crystalline compound. Urano-oxalic acid has not been isolated, but acid salts containing only a small amount of alkali are produced by the action of dilute hydrochloric acid on the urano-oxalates, the acid *ammonium* salt, formulated as $CO_2H\cdot CO_2\cdot U(C_2O_4)\cdot C_2O_4\cdot U(C_2O_4)\cdot CO_2\cdot CO_2\cdot NH_4,8H_2O$, forms microscopic prisms, and is converted directly into uranous oxalate by loss of a molecule of water when the alkali is completely removed. T. M. L.

Semialdehyde of β-Methyladipic Acid. By CARL D. HARRIES and OTTO SCHAUWECKER (*Ber.*, 1901, **34**, 1498—1501).—Citronellaldimethylacetal (Abstr., 1900, i, 331) is converted by oxidation with potassium permanganate into the *dimethyl semiacetal* of *β-methyladipic acid* (the dimethylacetal of 3-methylhexane-1-al-6-carboxylic acid), $CO_2H\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH(OMe)_2$, which is a faintly yellow liquid and boils at 149—152° under 7—8 mm. pressure. When preserved for some time, or allowed to remain in solution in acidified water, it yields the *aldehydo-acid*, $CO_2H\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CHO$, which is a colourless, refractive liquid, boils at 153—155° under 12 mm. pressure, is readily soluble in water, alcohol, or ether, and has a sp. gr. 1·0959 at 10°. It reduces Fehling's solution on boiling, and reddens magenta-sulphurous acid. The *silver* salt is a white, microcrystalline powder; the *semicarbazone*, $NH_2\cdot CO\cdot NH\cdot N:CH\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot CO_2H$, crystallises in white plates melting at 156—157°. A. H.

Influence of Molybdates and Tungstates on the Specific Rotation of Tartrates. By HERRMANN ITZIG (*Ber.*, 1901, **34**, 1372—1380).—It has been shown, in the case of tartaric acid (Abstr., 1900, i, 273), that a maximum value of the specific rotation is obtained when two alkali ions are present for every tartrate ion. This is also found to be the case with sodium hydrogen tartrate; the maximum value of $[\alpha]_D$ for $1C_4H_4O_6HNa$ is, with $\frac{1}{2}Na_2MoO_4$, 2 + 221·3; with $1/6(NH_4)_6Mo_7O_{24}$, + 456·7; with $\frac{1}{2}Na_2WO_4$, + 133·6; with $1/10Na_{10}W_{12}O_{41}$, + 220. The rotation is also raised by yellow, soluble molybdic acid, a maximum value, + 320·6, being obtained with $2MoO_3$.

As regards normal tartrates, the rotation of Rochelle salt is hardly affected by normal sodium molybdate, but it is raised largely by the salt $(NH_4)_6Mo_7O_{24}$, and to a less degree by $Na_{10}W_{12}O_{41}$, although in neither of these cases does the maximum correspond with a simple molecular ratio; it is also raised by yellow, soluble molybdic acid, a maximum value, +521·8, being obtained with $1C_4H_4O_6KNa : 1MoO_3$. The salt, $(NH_4)_6Mo_7O_{24}$, also raises the rotation of calcium tartrate in hydrochloric acid solution, and of tartar emetic; the rotation of the latter was depressed by normal sodium molybdate, but antimonious acid separated from the solution after a time.

Diacetyltartaric acid and glucose are not influenced, as regards their rotation, by molybdates or tungstates. C. F. B.

Oxidation of *l*-Arabonic Acid and *l*-Xylonic Acid. By OTTO RUFF (*Ber.*, 1901, **34**, 1362—1372. Compare Abstr., 1900, i, 139).—[With ADOLF MEUSSER.]—*l*-Arabinose was obtained from cherry gum and converted into calcium *l*-arabonate by Kiliani's method (Abstr., 1887, 229). This salt was oxidised with hydrogen peroxide and ferric acetate to *l*-erythrose, the *phenylbenzylhydrazone* of which melts at 105° (corr.), and has specific rotation $[\alpha]_D$ +32·8° in 5 per cent. alcoholic solution at 20°. From this hydrazone, formaldehyde liberates (Abstr., 1900, i, 77) *l*-erythrose, a colourless syrup with initial and final specific rotations $[\alpha]_D$ +2·40° and +21·5° respectively, in 5 per cent. solution at 20° (compare Weil, Abstr., 1900, i, 140); the yellow *osazone* of this tetrose melts at 164° (corr.). Bromine oxidises the crude erythrose in aqueous solution to l-*erythronic acid*, the *brucine* salt of this acid melts at 212°, and has $[\alpha]_D$ −30·7° and −28·4° at 20° in 9 and 4 per cent. solution respectively; the *lactone* melts at 104° (corr.) and has $[\alpha]_D$ 71·74° in 2·8 per cent. aqueous solution at 20°; the *phenylhydrazide* melts at 127°. Starting from a mixture of calcium *d*- and *l*-arabonates, an attempt was made to prepare *r*- or *dl*-derivatives. In the case of the phenylbenzylhydrazone, no *r*-compound could be obtained; from the concentrated solution of the two optical isomerides either could be crystallised at will by inoculating the solution with a crystal of the desired isomeride. The osazone obtained melted at the same temperature as the supposed *l*-erythrosazone, and a mixture of the two substances had still the same melting point, so that racemisation had probably taken place in the preparation of the osazone from the active erythrose. The yield of erythrose obtained by the method described is but small.

[With HUGO KOHN.]—Still smaller is the yield of tetrose obtained with *l*-xylose as a starting-point (prepared from wheat straw by Schulze and Tollens' method, Abstr., 1892, 1420). This was oxidised in aqueous solution with bromine to *l*-xylonic acid, the calcium salt of which was then oxidised with hydrogen peroxide and ferric acetate to l-*threose*. The *phenylbenzylhydrazone* of this tetrose melts at 194·5° (corr.); the *osazone* is identical with that obtained from *d*-erythrose (Abstr., 1900, i, 139); the sugar itself is reduced by sodium amalgam to *l*-erythritol (Maquenne, Abstr., 1900, i, 424), which was isolated in the form of its benzoic acetal, melting at 204—205°. C. F. B.

Condensation of Aldehydes. By ADOLF LIEBEN (*Monatsh.*, 1901, **22**, 289—313).—A summary of the work which has been carried out in the author's laboratory on this subject.

The first product of the condensation of 2 mols. of the same aldehyde, or of different aldehydes, is always an aldol in which the hydroxyl is in the β-position to the CHO group; the condensation takes place between the aldehyde group of one mol. and the α-carbon atom of the other. In the condensation of two aldehydes, both of which possess hydrogen atoms united to the α-carbon atom, it is generally found that the CHO group more readily condenses with a CH group than with a CH_2 group, and with the latter more readily than with a CH_3 group; thus from acetaldehyde and propaldehyde, the aldol

$$CH_3\cdot CH(OH)\cdot CHMe\cdot CHO$$

is obtained.

The aldols which possess a hydrogen atom attached to the α-carbon atom, may be converted into unsaturated aldehydes with elimination of water. Such aldols must be derived from an aldehyde, in which the CHO group is linked to CH_3 or CH_2. These are called by the author aldehydes of the first class. The second class of aldehydes, in which the CHO group is united to CH, form aldols [for example,

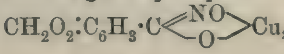
$$CHMe_2\cdot CH(OH)\cdot CMe_2\cdot CHO]$$

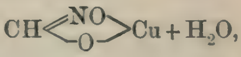
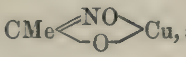
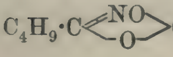
which cannot be converted into unsaturated aldehydes, as there is no hydrogen now attached to the α-carbon atom. In the third class of aldehydes, the CHO group is not linked to a carbon atom which is directly united to any hydrogen atoms; such aldehydes are formaldehyde, *iso*butyraldol, and benzaldehyde. They do not yield an aldol, but give Cannizzaro's reaction with alkaline condensing agents. Thus formaldehyde yields formic acid and methyl alcohol. The reaction is quantitatively represented by the equation $2CH_2O + KOH = HCO_2K + CH_3\cdot OH$, and is nearly complete after 11 days at a temperature of about 10°. Acetaldehyde and propaldehyde under similar conditions are converted chiefly into resins, only some 5 per cent. being transformed into acids. The author expresses the opinion that all aldehydes are capable of undergoing Cannizzaro's reaction, but that this reaction takes place so much more slowly than the aldol condensation that the former is practically entirely concealed.

The abnormal behaviour of *iso*butaldehyde in yielding octoglycol *iso*butyrate (Abstr., 1898, i, 353) or octoglycol and *iso*butyric acid is considered. The paper contains a list of the aldols so far prepared.

K. J. P. O.

New Reaction of Aldehydes. By ENRICO RIMINI (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 355—362).—The formation of the hydroxamic acids may be used as a means of detecting and identifying aldehydes. These acids, which are readily recognisable by the intense reddish-violet coloration which their solutions give with ferric chloride, may be formed by the action on the aldehydes of nitrohydroxylaminic acid, but in this case a nitrite is also produced, and the latter often changes the reactions of the hydroxamic acids. For the preparation of the latter, it is therefore better to employ benzenesulphohydroxamic acid, which in presence of an aldehyde splits up according to the equation $Ph\cdot SO_2\cdot NH\cdot OH = Ph\cdot SO_2H + NOH$, the oximido-residue combining with the aldehyde giving the corresponding hydroxamic acid. The reaction has been found to give positive results with a number of aldehydes, including formaldehyde, acetaldehyde, valeraldehyde, acraldehyde, citral, glyoxal, glyceraldehyde, benzaldehyde, piperonaldehyde, anisaldehyde, salicylaldehyde, furfuraldehyde, δ-aminovaleraldehyde, and formic acid. The aldehyde is dissolved in alcohol, a few c.c. of a $2N$ potassium hydroxide added, then the calculated quantity of the benzenesulphohydroxamic acid, and finally a few more c.c, of the potassium hydroxide solution. The liquid is left for a short time, after which the alcohol is distilled off. The hydroxamic acids can readily be separated from the solution in the form of their copper salts, which are insoluble blue or green precipitates.

Copper piperonalhydroxamate,  $CH_2O_2{:}C_6H_3\cdot C{<}^{NO}_{O}{>}Cu$, is obtained as a pale green precipitate.

The *copper* salts of formalhydroxamic acid,  $CH{<}^{NO}_{O}{>}Cu + H_2O$, acetalhydroxamic acid,  $CMe{<}^{NO}_{O}{>}Cu$, and *iso*valeralhydroxamic acid,  $C_4H_9\cdot C{<}^{NO}_{O}{>}Cu$, were analysed.

T. H. P.

Succindialdehyde. By CARL D. HARRIES (*Ber.*, 1901, **34**, 1488—1498).—*Succindialdehyde*, $CHO\cdot CH_2\cdot CH_2\cdot CHO$, can readily be prepared by passing nitrous fumes through succindialdoxime suspended in water, the neutralised liquid is then evaporated in a vacuum, and the residue distilled in vacuum. The dialdehyde is a hard, glassy mass of sp. gr. 1·23 at 19°, which becomes viscid at 25° and readily mobile at 70°, and boils at 65—66° under 11 mm. and at 160—170° under atmospheric pressure without decomposition. On standing in the air, it becomes yellow and viscid. It is sparingly soluble in water, ether, or benzene, readily so in hot alcohol; the vapour has a penetrating odour and an irritating effect on the skin and mucous membrane. It reduces alkaline Fehling's solution strongly in the cold, and produces a blue coloration with magenta and sulphurous acid. The aldehyde appears to exist in two forms, one of which is readily soluble in water and is perhaps the hydrate, whilst the solid form described above is anhydrous and sparingly soluble. The *monohydrate* is a thick liquid and boils at about 55° under 12 mm. pressure. The aldehyde is stable towards dilute acids, but becomes dark coloured and resinous with concentrated acids. It is, however, at once converted by alkalis into a yellow, amorphous mass, and reacts explosively with concentrated aqueous potash. It is converted by heating with water at 180° into furfuran, by boiling with ammonia and acetic acid into pyrrole, and by heating with phosphorus trisulphide into thiophen.

Succintetramethylacetal, $C_2H_4[CH(OMe)_2]_2$, obtained by acting on the aldehyde with formimino-ether hydrochloride, has a sp. gr. 0·9897 at 19°, and boils at 201—202° under 772 mm. pressure. Dilute hydrochloric acid in the cold converts it into the dialdehyde. The *hydrogen sulphite*, $C_2H_4[CH(OH)\cdot SO_3Na]_2$, crystallises in slender needles. The diphenylhydrazone, which was previously obtained by Ciamician and Zanetti from the dioxime (Abstr., 1890, 1120) is readily prepared by the direct action of phenylhydrazine acetate. The *monobromophenylhydrazone*, $CHO\cdot CH_2\cdot CH_2\cdot CH{:}N\cdot NH\cdot C_6H_4Br$, crystallises in greenish plates melting at 135—136°. The *dibromophenylhydrazone*, $C_2H_4(CH{:}N_2H{\cdot}C_6H_4Br)_2$, forms square, yellow crystals melting at 140—145° and is very unstable. The aldehyde condenses with *o*-phenylenediamine, forming a compound which melts at 175—177°, the nature of which has not yet been determined.

When succindialdoxime is treated with a solution of hydrogen chloride in methyl alcohol, it yields a small amount of succintetramethylacetal, together with a larger amount of *succinmonoaldehydoacetal imino-ether*, $CH(OMe)_2{\cdot}CH_2{\cdot}CH_2{\cdot}C(OMe){:}NH$, which boils at 82—83° under 20—21 mm. pressure, and has basic properties. *Dibenzoylsuccindialdoxime*, $C_2H_4(CH{:}N{\cdot}OBz)_2$, crystallises in indistinct plates melting at 152°. *Dimethoxysuccindialdoxime* is obtained by the action of sodium methoxide and methyl iodide, in the form of a brown oil, which with hydrogen chloride and methyl alcohol yields the *monooxime methyl ether* derivative of the monoacetal of succinic acid,

$$CH(OMe)_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}NOMe,$$

which boils at 180—200°. On treatment with hydrochloric acid, this is converted into the corresponding *derivative* of the aldehyde, $CHO{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}N{\cdot}OMe$, which boils at 67° under 10 mm. pressure.

A. H.

Symmetrical α-Diketones of the Aliphatic Series. By GIACOMO PONZIO (*J. pr. Chem.*, 1901, [ii], **63**, 364—369. Compare Abstr., 1897, i, 317; 1899, i, 111, and 1900, i, 588).—By the action of concentrated nitric acid on ketone alcohols of the type $R{\cdot}CO{\cdot}CH(OH){\cdot}R$, a number of fatty α-diketones are prepared. They are all yellow liquids, lighter than water, which distil without decomposing, forming a yellow vapour, and readily distil in steam.

Diethyl diketone (dipropionyl) (Abstr., 1897, i, 317) was isolated from the product of the action of nitric acid on dipropioin by distillation in steam, and then converted into the *oxime*, $C_2Et_2(N{\cdot}OH)_2$, which crystallises from benzene in white needles melting at 185°.

Dipropyl diketone (dibutyryl) was obtained together with *dinitropropane*, which dissolves in aqueous potassium carbonate, forming a yellow solution. The *potassium* salt, $C_3H_5O_4N_2K$, of the latter crystallises in yellow plates. *Dipropyl diketoxime*, $C_2Pr^{\alpha}{}_2(NOH)_2$, forms white needles, melting at 175°. *Diïsopropyl diketoxime*, $C_2Pr^{\beta}{}_2(NOH)_2$, prepared in an analogous manner to the oximes previously mentioned, forms white needles which melt at 163—164°. *Diïsobutyl diketoxime*, $(CH_2Pr^{\beta})_2{\cdot}C_2(NOH)_2$, crystallises in silky, lustrous needles which melt at 195°.

K. J. P. O.

Synthetic Action of Yeast Maltase. By ARTHUR CROFT HILL (*Ber.*, 1901, **34**, 1380—1384).—The author disputes Emmerling's conclusions (this vol., i, 258) that, in the (reversed) hydrolysis of dextrose (Trans., 1898, **73**, 634), (1) the sugar formed is not fermentable; (2) the osazone isolated was *iso*maltosazone.

C. F. B.

Cellulose Xanthates. By CHARLES F. CROSS and EDWARD J. BEVAN (*Ber.*, 1901, **34**, 1513—1520).—This is a general review of experimental results which the authors intend publishing later in detail. To form the cellulose xanthates, the best proportion of the ingredients to use is that given by $C_6H_{10}O_5 : 2NaOH : CS_2$; the xanthate is derived from a hydrate, such as $C_6H_{10}O_5,H_2O$, the second mol. of sodium hydroxide becoming attached to the cellulose complex to form a compound of the type $NaS{\cdot}CS{\cdot}O{\cdot}C_6H_9O_4,NaOH$. In the xanthate initially formed, the cellulose is present as a C_6 complex, and the product is not precipitated by neutral dehydrating agents even after acidification; after 24 hours a C_{12} complex is formed, this being the principal ingredient of the so-called "viscose" solution. It is stable for some days, but at the period of coagulation changes into a C_{24} xanthate,

$$NaS{\cdot}CS\ O{\cdot}C_{24}H_{39}O_{19},NaOH,$$

which is insoluble in water, soluble in dilute alkalis, and is precipitated from its original solution on adding acid.

For the methods of purification and analysis used, the original should be consulted; the percentage of alkali (NaOH), sulphur, and sodium was determined in the various cases. In determining the alkali, advantage was taken of the fact that it is not removed from combination with the ·CS·S group of the xanthate by dilute acetic acid, although dilute sulphuric acid effects complete decomposition. As a check on this method of determining the combined alkali, that based on the equation $2NaS{\cdot}CS{\cdot}OR + I_2 = (OR{\cdot}CS{\cdot}S{\cdot})_2 + 2NaI$, using a normal solution of iodine, was employed, concordant results being obtained by the two methods. W. A. D.

Oxycellulose and Hydrocellulose. By J. J. Murumow, J. Sack, and Bernhard Tollens (*Ber.*, 1901, **34**, 1427—1434).—The oxycellulose obtained by the action of potassium chlorate and hydrochloric acid on cotton wool, when boiled with lime and water, yields cellulose, *iso*saccharinic acid, and dihydroxybutyric acid. In this respect, it resembles the oxycelluloses prepared from pine wood and nitric acid, from cotton wool, bromine, and calcium carbonate, and from cotton wool and nitric acid (see von Faber and Tollens, Abstr., 1899, i, 854). Products very similar to, and possibly identical with, those yielded by the oxycelluloses are obtained when the hydrocellulose prepared by digesting cotton wool with sulphuric acid of sp. gr. 1·52—1·54 is boiled with lime and water. T. H. P.

Cellulose, Oxycellulose, Hydrocellulose, the Pectins, and Tragacanth. By Bernhard Tollens (*Ber.*, 1901, **34**, 1434—1441).—The author divides these compounds into the following classes: (1) celluloses; (2) hydrated celluloses, that is, hydrocelluloses and hemicelluloses, which are non-reducing; (3) celluloses containing carboxyl groups, as, for example, the pectic acids; (4) celluloses with carboxyl and reducing (carbonyl) groups, to which belong the oxycelluloses and celloxin.

The properties and relations of these various classes of compounds are discussed. The author considers that the formula of hydralcellulose (Bumcke and Wolffenstein, Abstr., 1899, i, 852) is not ascertained with sufficient certainty to allow of any conclusions concerning other oxycelluloses being drawn, and he continues to regard the oxycelluloses as real oxidation products of cellulose.

Contrary to the views of Hilger and Dreyfus (Abstr., 1900, i, 379) the author holds that oxybassorin and also tragacanth contain carboxyl groups. From the products of hydrolysis of a sample of vermicelli tragacanth, the first-named authors (*loc. cit.*) obtained by crystallisation only arabinose; this sugar was previously obtained in this way by Widtsoe and Tollens (Abstr., 1900, i, 207), who also isolated fucose by precipitation as phenylhydrazone and decomposition of the latter by benzaldehyde. T. H. P.

[**Properties and Composition of Glycogen.**] By JOSEPH NERKING (*Pflüger's Archiv*, 1901, 85, 313—319, 320—329).—See this vol., ii, 462.

Oxidation of Compounds containing Nitrogen. By DANIEL VORLÄNDER (*Ber.*, 1901, 34, 1637—1642. Compare this vol., i, 444).—The ready oxidation of various organic substances containing nitrogen is shown to depend on (1) the unsaturated character of tervalent nitrogen, and (2) on the presence of a hydrogen atom in position 3 (*loc. cit.*). Neither of these conditions alone suffices. Thus, ammonia and azobenzene both contain tervalent nitrogen, but no hydrogen atom in position 3, and cannot be oxidised easily. On the other hand, alkyl (alphyl) amines, hydroxylamine, and hydrazine, in which such a hydrogen atom is present, are easily oxidised. In α-ethylhydroxylamine, this hydrogen atom is replaced, and consequently this substance is stable to Fehling's solution, whilst β-ethylhydroxylamine is readily oxidised. In salts of nitrogen bases, the nitrogen is saturated, and the compounds again become stable to oxidising agents.

Anilinodiacetic acid, $N^{III}Ph(CH_2\cdot CO_2H)_2$, and phenylglutaric acid, $CHPh(CH_2\cdot CO_2H)_2$, are contrasted. The former, with the hydrogen atom in position 3 to the unsaturated nitrogen atom, is immediately oxidised by potassium permanganate, and gives a colour reaction with ferric chloride, whilst the latter with a saturated carbon atom is stable under these conditions. K. J. P. O.

A new Glycine Anhydride. By LUIGI BALBIANO (*Ber.*, 1901, 34, 1501—1504. Compare Abstr., 1900, i, 632).—The examination of the compound $C_{22}H_{34}O_{13}N_{10}$, which was previously described, shows that it is in reality an anhydride of glycine, has the formula C_2H_3ON, and is completely converted into glycine by hydrolysis. It appears, however, to differ from the anhydride already described by Curtius and Goebel (Abstr., 1888, 576) which, however, is present in the washings obtained from the crude compound.

Small amounts of glycollic acid can be estimated in presence of glycine by evaporating with hydrochloric acid and extracting the dry mass with a mixture of alcohol and ether (1 of alcohol to 10 of ether) which dissolves the glycollic acid. A. H.

Action of Hydrofluosilicic Acid on Potassium Ferricyanide. By J. MATUSCHEK (*Chem. Zeit.*, 1901, 25, 327—328. Compare this vol., i, 262).—Solutions of hydrofluosilicic acid and of potassium ferricyanide react with one another, even in the absence of air, yielding a precipitate of Berlin blue, probably formed according to the equation $14K_3FeC_6N_6 + 21H_2SiF_6 + 3H_2O = 21K_2SiF_6 + 2Fe_4(FeC_6N_6)_3$

$+48HCN+3O$. The reaction is not so delicate as with the ferrocyanide. J. J. S.

Influence of Sunlight on Aqueous Solutions of Potassium Ferricyanide. By J. Matuschek (*Chem. Zeit.*, 1901, **25**, 411—412).—Dilute aqueous solutions of potassium ferricyanide are decomposed by sunlight even in the absence of air, ferric hydroxide being precipitated. When the concentrations increase in the form of an arithmetical series, it is found that the amounts of precipitate form a decreasing arithmetical series. J. J. S.

Ferricyanides of the Alkali Earths. By Th. Fischer and P. Müller (*Chem. Zeit.*, 1901, **25**, 321—322).—Crystals of barium ferricyanide, $Ba_3Fe_2C_{12}N_{12},20H_2O$, were prepared by neutralising the corresponding acid with barium carbonate and evaporating the solution to crystallisation. The *strontium* salt, $Sr_3Fe_2C_{12}N_{12},14H_2O$, forms well-developed, reddish-brown prisms. The *calcium* salt crystallises with $12H_2O$ in small, glistening needles, and its aqueous solution is decomposed when warmed. The *magnesium* salt forms reddish-black, nodular masses, and when dried over sulphuric acid contains $10H_2O$; its aqueous solution is decomposed when heated. The following salts have also been prepared:—$BaKFeC_6N_6,4H_2O$, hexagonal prisms; $SrKFeC_6N_6,3H_2O$, deep ruby red prisms; $CaKFeC_6N_6,3H_2O$, deep red plates much more stable than the simple calcium salt;

$$MgKFeC_6N_6,4H_2O,$$

nodular masses; $BaNaFeC_6N_6,3H_2O$, brownish-red lamellæ; $SrNaFeC_6N_6,3H_2O$; $CaNaFeC_6N_6,5H_2O$; $MgNaFeC_6N_6,6H_2O$; $BaNH_4FeC_6N_6,4H_2O$; $SrNH_4FeC_6N_6,3H_2O$; $CaNH_4FeC_6N_6,3H_2O$; $MgNH_4FeC_6N_6,6H_2O$. J. J. S.

Double Thiocyanates and the Ferric Thiocyanate Reaction. By Arthur Rosenheim and Robert Cohn (*Zeit. anorg. Chem.*, 1901, **27**, 280—303).—Three series of mercury double thiocyanates are known. The *monothiocyanates*, $HgSCNCl$,$HgSCNBr$, and $HgSCN{\cdot}OAc$, are described. Direct physical evidence of the presence of the complex cation, $HgSCN$, in these salts cannot be obtained on account of their slight solubility. When, however, they are treated with a solution of alkali chromate or dichromate, bright yellow precipitates are obtained which contain the thiocyanate radicle chemically combined, and the authors consider this to be evidence of the presence of the cation $HgSCN$ in these salts.

The *mercury trithiocyanates*, $KHg(SCN)_3$, $NH_4Hg(SCN)_3$, and $Ba[Hg(SCN)_3]_2,2H_2O$, are well crystallised salts, insoluble in cold water, but easily soluble in hot water whereby they are decomposed into mercury thiocyanate and the tetrathiocyanate.

Mercury tetrathiocyanates.—The *potassium* salt, $K_2Hg(SCN)_4$, obtained by crystallising a mixture of the constituent salts, crystallises in white needles and is easily soluble in water and alcohol. The *sodium* and *barium* salts are similar. The *copper* salt, $CuHg(SCN)_4$, obtained by treating a solution of the alkali salt with copper chloride or nitrate, crystallises from boiling water in intensely green, microscopic tablets and is insoluble in cold water or alcohol. The electrical conductivity of both the trithiocyanates and the tetrathiocyanates shows that they are salts of a complex acid, as also does their behaviour in Nernst's apparatus for demonstrating the movement of the ions.

Cobalt thiocyanate, $Co(SCN)_2,3H_2O$, obtained by dissolving cobalt carbonate in thiocyanic acid, crystallises in violet, rhombic tablets [$a:b:c = 1{\cdot}2302:1:0{\cdot}5824$], and gives a blue solution in water and alcohol which turns pink on dilution. The *double* salts, $K_2Co(SCN)_4,4H_2O$; $Na_2Co(SCN)_4,8H_2O$ $(NH_4)_2Co(SCN)_4,4H_2O$, and $BaCo(SCN)_4,8H_2O$, are obtained by adding the corresponding thiocyanate to a solution of the cobalt salt. They crystallise in beautiful, dark blue needles, can be recrystallised from water or alcohol, are soluble in methyl, ethyl, or amyl alcohol, acetone or wet ether, and give deep blue solutions which on dilution turn bright rose colour. The *silver* salt, $Ag_2Co(SCN)_4$, is obtained by titurating a concentrated alcoholic solution of the potassium salt with freshly precipitated silver thiocyanate.

Nickel thiocyanate, $Ni(SCN)_2,1\frac{1}{2}H_2O$, is a yellowish-brown, crystalline powder and gives a green solution in water. The *potassium*, *sodium*, and *ammonium* double salts are crystalline, hygroscopic salts easily soluble in water or hot alcohol with a green colour, and by solution in water are decomposed into their components. *Barium* and *silver* salts cannot be obtained. They are insoluble in most organic solvents and do not behave like salts of a complex acid. This difference in the behaviour of the cobalt and nickel salts explains Vogel's qualitative test for cobalt in the presence of nickel.

Potassium chromium thiocyanate, $K_2Cr(SCN)_6,4H_2O$, and the sodium salt, with $12H_2O$, obtained according to Roesler's method (*Annalen*, 1867, **141**, 185), have an electrical conductivity which points to their being salts of the complex group $Cr(SCN)_6$.

An examination of the iron double thiocyanates shows that two series of salts are formed, namely, ferrihexathiocyanates and ferrohexathiocyanates, which correspond respectively with the ferri- and ferro-cyanides.

Sodium ferrithiocyanate, $Na_3Fe(SCN)_6,12H_2O$, obtained by allowing a solution of the constituent thiocyanates to crystallise over sulphuric acid, forms dark green, hexagonal or rhombic crystals, is decomposed by alkali hydroxides with the formation of ferric hydroxide, dissolves in absolute alcohol to a violet solution resembling permanganate, from which it separates without decomposition; with water, it yields the well known deep red solution, and is partially decomposed, and with ether is decomposed into its constituents, whereby the ferric thiocyanate is dissolved. The *potassium* and *ammonium* salts crystallise with $4H_2O$.

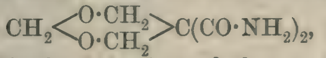
Sodium ferrothiocyanate, $Na_4Fe(SCN)_6,12H_2O$, obtained by dissolving ferrous carbonate in thiocyanic acid and adding to the solution sodium thiocyanate, crystallises in colourless tablets, dissolves in water and alcohol with a bright rose coloration, and is oxidised by exposure to the air. The *potassium* and *ammonium* salts are bright red, micro-crystalline salts and are extremely hygroscopic.

An examination of the ferrihexathiocyanates in Nernst's apparatus shows that the violet absolute alcoholic solution contains the complex

$Fe(SCN)_6$, whilst the blood red solutions do not contain a complex anion. These results show that the red coloration obtained on adding a ferric salt to a thiocyanate is due to the presence of ferric thiocyanate, and not to the formation of a complex double salt.

Potassium aluminium thiocyanate, $K_3Al(SCN)_6,4H_2O$, obtained in a similar manner to the iron salt, crystallises in colourless crusts, is very hygroscopic, and easily soluble in water or alcohol. E. C. R.

Methylenemalonamide and Methylenebiuret. By Hugo Schiff (*Annalen*, 1901, **316**, 242—249).—*Methylenemalonamide*, $C_6H_{10}N_2O_4$, obtained by the action of formaldehyde on malonamide, has one or other of the following formulæ, $CH_2{:}C(CO\cdot NH\cdot CH_2\cdot OH)_2$ or



$CH_2<\begin{matrix}O\cdot CH_2\\ O\cdot CH_2\end{matrix}>C(CO\cdot NH_2)_2$, the second being more in accordance with the behaviour of the compound. The substance slowly evolves ammonia when treated with cold potassium hydroxide, it gives the biuret reaction, and when treated with mercuric nitrate and potassium hydroxide, yields three *mercurides*, having the following composition, $Hg(C_6H_9O_4N_2)_2$, $Hg(C_6H_8O_4N_2)$ and $Hg_2(C_6H_7O_4N_2)_3$.

Methylenebiuret, $CH_2[O\cdot CH_2\cdot N(CO\cdot NH_2)_2]_2$, prepared by gradually adding formaldehyde to a saturated alcoholic solution of biuret heated at 50° is obtained as an amorphous, colourless, pasty mass; it gives the biuret reaction and unstable *mercurides* varying in composition from $Hg_3(C_7H_{11}O_6N_6)_2$ to $Hg_2(C_7H_{10}O_6N_6)$. The paper includes a description of a method for estimating mercury in organic compounds. G. T. M.

Methyl Cyanide as a Catalytic Reagent; and a Criticism of J. U. Nef's views on the Frankland, Wurtz, and Conrad Reactions. By Arthur Michael (*Amer. Chem. J.*, 1901, **25**, 419—430).—If, in the preparation of hydrocarbons by the action of sodium on alkyl haloids, a few drops of acetonitrile are added, the necessity for heating in a sealed tube is avoided, and the yield of the product is increased. On addition of acetonitrile to a well-cooled mixture of methyl iodide and sodium, an energetic reaction occurs; when ethyl or propyl iodide is treated at the ordinary temperature with sodium in presence of the nitrile, a good yield of butane or *n*-hexane is obtained. Allyl iodide, *iso*propyl iodide, trimethylene bromide and benzyl chloride behave in a similar manner. The acetonitrile may be replaced by propionitrile or butyronitrile, which, however, exert a less marked influence; benzonitrile and phenylacetonitrile cause no acceleration of the reaction.

When ethylene bromide is boiled with zinc-sodium, no action takes place; in presence of ethyl oxalate, however, at a temperature of 40°, gas is rapidly evolved and ethyl bromide produced.

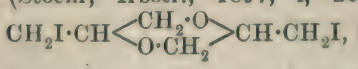
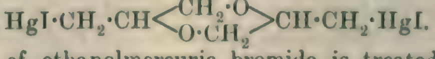
If zinc ethyl iodide, prepared by heating a mixture of zinc, ethyl iodide, and ether on the water-bath, is treated with an ethereal solution of benzoyl chloride, phenyl ethyl ketone is formed, together with a product boiling at 193—196° under 9 mm. pressure, and a small quantity of a white, crystalline substance. The author has also studied the action of zinc ethyl iodide on ethyl malonate, and obtained ethyl ethylmalonate and a little ethyl diethylmalonate; the last-mentioned substance forms an additive compound with zinc ethyl iodide.

The paper concludes with a criticism of Nef's views on the Frankland, Wurtz, and Conrad reactions. E. G.

Constitution of the Compounds of Ethylene and Allyl Alcohol with Mercuric Salts. By JULIUS SAND (*Ber.*, 1901, **34**, 1385—1394. Compare Abstr., 1900, i, 384, 386, 618).—Ethanolmercuric iodide, $OH\cdot CH_2\cdot CH_2\cdot HgI$, was obtained in the same manner as the corresponding chloride and bromide. When it is boiled with iodine, either in aqueous potassium iodide or in alcoholic solution, mercuric iodide and glycol iodohydrin (Henry, *Bull. Acad. roy. Belg.*, 1889, [iii], **18**, 182) are formed. The latter boils at 78° under 16 mm. pressure; when heated with quinoline at 100°, it forms a yellow *quinolinium iodide*, $OH\cdot CH_2\cdot CH_2\cdot C_9H_7NI$, which melts at 157°, and can be converted into the corresponding *chloride*, a colourless, deliquescent substance melting at 122°. Ethanolmercuric iodide forms a *benzoyl* derivative melting at 118°; this, unlike the parent substance, is not decomposed readily by hydrochloric acid with evolution of ethylene. Acetic anhydride does not convert ethanolmercuric bromide into a corresponding acetyl derivative; monobromomercuriacetic acid, melting at 117—118°, is obtained instead.

Ethyl ether mercuric iodide, $O(CH_2\cdot CH_2\cdot HgI)_2$, was obtained by passing ethylene into aqueous mercuric sulphate, dissolving the precipitate in aqueous potassium hydroxide, and precipitating with potassium iodide. It is an oil which decomposes when distilled even under diminished pressure. With quinoline, it forms a reddish-yellow *monoquinolinium* and a red *diquinolinium* salt, $I\cdot C_9H_7N\cdot CH_2\cdot CH_2\cdot O\cdot CH_2\cdot CH_2I$ and $O(CH_2\cdot CH_2\cdot C_9H_7NI)_2$, melting at 176° and 254°, in the latter case with decomposition, and respectively more and less soluble in alcohol.

Propylene glycol mercuric iodide, $OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot HgI$, does not crystallise readily; iodine converts it even at 40° into a liquid iodohydrin, and it forms a *dibenzoyl* derivative which melts at 100° and is stable to hydrochloric acid, although acetic acid decomposes the parent substance into allyl alcohol and mercuric salt.

The substance described as propenolmercuric iodide, $OH\cdot CH_2\cdot CH\colon CH\cdot HgI$, is obtained by treating aqueous mercuric nitrate solution alternately with potassium hydroxide and allyl alcohol, precipitating with potassium iodide, and recrystallising from 20 per cent. aqueous potassium hydroxide. When heated with iodine and benzene at 140°, it yields mercuric iodide and di-epiiodohydrin (Stoehr, Abstr., 1897, i, 262). As this has the constitution  $CH_2I\cdot CH{<}\genfrac{}{}{0pt}{}{CH_2\cdot O}{O\cdot CH_2}{>}CH\cdot CH_2I$, the original iodide must have been *dipropylene oxide mercuric iodide*,  $HgI\cdot CH_2\cdot CH{<}\genfrac{}{}{0pt}{}{CH_2\cdot O}{O\cdot CH_2}{>}CH\cdot CH_2\cdot HgI$.

When an alkaline solution of ethanolmercuric bromide is treated with alkaline stannous chloride solution, a volatile, poisonous mercury compound is formed, probably *mercury dihydroxydiethyl*, $Hg(CH_2\cdot CH_2\cdot OH)_2$. C. F. B.

Hydrogenation of Aromatic Hydrocarbons. By PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1901, **132**, 1254—1257).—The action of reduced nickel below 250° on mixtures of aromatic hydrocarbons and hydrogen (this vol., i, 195 and 263) is simple in the case of benzene and its methyl derivatives, and the sole product is the corresponding *cyclo*hexane, but if ethyl, propyl, *iso*propyl, and other longer chains have been inserted in the benzene molecule the reaction is more complicated, and small quantities of lower homologues are formed with the principal product. *cyclo*Hexane itself has an odour recalling those of chloroform and oil of roses; it melts at 6·5°, boils at 81° under 755 mm. pressure, and has a sp. gr. 0·7808 at 18·7°. The other *cyclo*hexanes prepared were as follows:

	B. p. corr.	Sp. gr. at 0°/4°.
Methyl*cyclo*hexane	100·1°	0·7859
1 : 2-Dimethyl*cyclo*hexane	126	0·8008
1 : 3-Dimethyl*cyclo*hexane	121	0·7874
1 : 4-Dimethyl*cyclo*hexane	120	0·7866
Ethyl*cyclo*hexane	130	0·8025
1 : 3 : 5-Trimethyl*cyclo*hexane	137—139	0·7884
1 : 3 : 4-Trimethyl*cyclo*hexane	143—144	0·8052
1-Methyl-4-ethyl*cyclo*hexane	150	0·8041
Propyl*cyclo*hexane	153—154	0·8091
1-Methyl-4-*iso*propyl*cyclo*hexane	169—170	0·8132

The sp. gr. is less than that of the corresponding benzene hydrocarbon, but the difference is lower the more complex the molecule.

Styrene in presence of nickel is completely converted into ethyl*cyclo*hexane. Further, reduced copper at 180° in presence of hydrogen converts it into ethylbenzene (compare Abstr., 1900, i, 469), whilst with reduced cobalt, intermediate in energy between copper and nickel, the product is a mixture of ethylbenzene and ethyl*cyclo*hexane.

Under the same conditions, the quadrivalent terpenes, such as limonene, sylvestrene, and terpinene, yield 1-methyl-4-*iso*propyl*cyclo*hexane, as also does menthene. Terebenthene and *l*-camphene, on the other hand, yield two isomeric hydrocarbons of the composition $C_{10}H_{18}$. The product from the first boils at 166° (corr.), and has a sp. gr. 0·862 at 0°/4°, and that from the second boils at 164—165° (corr.), and has a sp. gr. 0·849 at 0°/4°.

Naphthalene at 200° yields solely the tetrahydride, $C_{10}H_{12}$, boiling at 205° (corr.), and having a sp. gr. 0·9825 at 0°/4°. Acenaphthene behaves similarly, but the product boils at 254° (corr.), and is identical with the reduction product obtained by Bamberger and Lodter by the action of hydrogen iodide. C. H. B.

Electrochemical reduction of Aromatic Mononitro-compounds to Amines. By KARL ELBS and F. SILBERMANN (*Zeit. Elektrochem.*, 1901, **7**, 589—591).—At a zinc cathode or in presence of a zinc salt, nitrobenzene and its homologues are reduced mainly to the corresponding amines. Similar results are obtained with a lead cathode, the yields being rather better (80 to 90 per cent.). T. E.

Aromatic Nitro-compounds. XIV. Action of Potassium Cyanide on 1-Chloro-2 : 4-dinitrobenzene in Alcoholic Solution. By W. J. van Heteren (*Rec. Trav. Chim.*, 1901, **20**, 107—110. Compare Lobry de Bruyn, Abstr., 1885, 656, 657 ; 1895, i, 654).—When 1-chloro-2 : 4-dinitrobenzene is heated with aqueous potassium cyanide in ethyl alcoholic solution at 40°, the temperature rises to 60°, and a dark-brown, amorphous precipitate is formed, from which a small quantity (5 per cent.) of a *chloronitrocyanoethoxybenzene* (probably $OEt:CN:NO_2:Cl = 1:2:3:4$ or $1:2:3:6$, compare *loc. cit.*) can be isolated ; it separates from alcohol in nearly colourless crystals and melts at 112°. Using methyl alcohol, the analogous *chloronitrocyanomethoxybenzene* is obtained in similar yield ; it crystallises from alcohol in nearly colourless leaflets and melts at 163°. W. A. D.

Aromatic Nitro-compounds. XV. Replacement of the Nitro-group by Methoxyl in 1-Chloro-3 : 5-dinitrobenzene. By A. C. de Kock (*Rec. Trav. Chim.*, 1901, **20**, 111—114).—Details are given for preparing 3 : 5-dinitroaniline from trinitrobenzene by reduction with ammonium sulphide ; 1-chloro-3 : 5-dinitrobenzene, obtained from it by Sandmeyer's reaction, when boiled with sodium methoxide in methyl alcoholic solution for an hour, yields about 10 per cent. of its weight of 3-*chloro*-5-*nitro*-1-*methoxybenzene*, which separates from dilute alcohol in small, white crystals and melts at 91°. No well-defined product could be obtained by using sodium ethoxide in ethyl alcoholic solution instead of the methoxide in this interaction. W. A. D.

Aromatic Nitro-compounds. XVI. Comparative Study of the three Dinitrobenzenes. III. Action of Sodium Monosulphide. By Cornelis A. Lobry de Bruyn and J. J. Blanksma (*Rec. Trav. Chim.*, 1901, **20**, 115—120. Compare Abstr., 1900, i, 226).—When *o*-dinitrobenzene is boiled with an alcoholic solution of sodium monosulphide (1 mol.), *o*-nitrothiophenol seems to be formed, but cannot be isolated ; using 2 mols. of the monosulphide, 1 : 1′-dinitrodiphenylsulphide is formed, which is oxidised at the ordinary temperature by nitric acid of sp. gr. 1·5 to the *sulphoxide*, $(NO_2 \cdot C_6H_4)_2SO$. This separates from alcohol in yellow crystals, melts at 184°, and is further oxidised by boiling nitric acid to 1 : 1′-dinitrodiphenylsulphone (Gericke, *Annalen*, 1856, **100**, 211 ; Colby and McLoughlin, Abstr., 1887, 371).

In alcoholic solution, sodium monosulphide principally reduces *m*-dinitrobenzene to *m*-nitroaniline, but di-*m*-nitroazoxybenzene is also formed along with sodium thiosulphate and amorphous products (compare this vol., i, 461) ; from *p*-dinitrobenzene, di-*p*-nitroazobenzene is formed along with an amorphous powder insoluble in glacial acetic acid. W. A. D.

Substitutions and Transformations effected by Sodium Disulphide. By J. J. Blanksma (*Rec. Trav. Chim.*, 1901, **20**, 121—140).—A full account of work formerly dealt with in brief (Abstr., 1900, i, 226 and 442) ; in all the following cases, the substance taken was boiled with alcoholic sodium disulphide for periods varying from a few minutes to one or two hours. *p*-Chloronitrobenzene and *p*-iodonitrobenzene both yield di-*p*-nitrophenyl disulphide which melts at 170°, the melting point not being raised by several crystallisations, although when prepared from *p*-nitrothiophenol it melts, as stated by Willgerodt (Abstr., 1885, 519), Bamberger and Kraus (Abstr., 1896, i, 218), and Kehrmann and Bauer (Abstr., 1897, i, 27), at 181°; it is remarkable for exploding to a fine powder at 134°, this temperature being evidently a point of transition of crystalline form. On oxidation with nitric acid of sp. gr. 1·5, it yields *p*-nitrobenzenesulphonic acid, which forms long hygroscopic crystals, melts at 95°, and yields a *sulphochloride* crystallising from ether and melting at 76°, and a *sulphonamide* crystallising from water and melting at 178°; Limpricht (this Journal, 1875, 1027) describes the sulphochloride as a red oil and the sulphonamide as melting at 131°.

1 : 4-Dichloro-2-nitrobenzene yields 4 : 4′-*dichloro*-2 : 2′-*dinitrodiphenyl disulphide* which melts at 212°, and was formerly described by Beilstein and Kurbatow (Abstr., 1878, 139) as chloronitrophenylmercaptan; on oxidation with nitric acid, it yields 4-*chloro*-2-*nitrobenzenesulphonic acid*, the *sulphochloride* of which forms white crystals and melts at 78—79°. 4 : 4′-*Dibromo*-2 : 2′-*dinitrodiphenyl disulphide*, obtained from 1 : 4-dibromo-2-nitrobenzene, forms yellow crystals, melts at 174°, and yields on oxidation a hygroscopic 4-*bromo*-2-*nitrobenzenesulphonic acid* melting at 126°; the *sulphochloride* is white and melts at 100°. 2 : 2′-*Dinitro*-5 : 5′-*dichlorodiphenyldisulphide*, obtained from 1-chloro-3 : 4-dinitrobenzene as principal product, forms yellow crystals and melts at 171°; a small quantity of a *substance* melting at 151° is also formed.

Allyl disulphide is a yellow oil which boils at 100° under 80 mm., and at 174° with decomposition under the ordinary pressure; it has a sp. gr. 1·010 at 15°, and combines additively with 2 mols. of bromine to form a thick oil which is decomposed by atmospheric moisture.

Ethylene bromide yields a white, amorphous *compound*, $(C_2H_4S_2)_n$, which melts at 113°, and is not identical with Fasbender's diethylene tetrasulphide (Abstr., 1888, 805), although, like the latter, it yields ethylenedisulphonic acid on oxidation with nitric acid.

Fluorescein chloride yields a *disulphide*, $C_{20}H_{10}O_3S_2$, as a greyish powder which does not melt at 300°. W. A. D.

Reducing Action of Sodium Disulphide. Preparation of Di-*m*-nitroazoxybenzene and of Di-*p*-nitroazobenzene. By J. J. Blanksma (*Rec. Trav. Chim.*, 1901, **20**, 141—143).—On boiling *m*-dinitrobenzene (2 mols.) with sodium disulphide in alcoholic solution, sodium thiosulphate and a nearly theoretical yield of di-*m*-nitroazoxybenzene are obtained; the abnormal action of sodium monosulphide on *m*-dinitrobenzene (de Bruyn and Blanksma, this vol., i, 460) is probably due to the monosulphide used being in this case initially transformed into sodium disulphide and hydroxide, the latter being responsible for the amorphous substance formed. In the case of *p*-dinitrobenzene, di-*p*-nitroazobenzene is the principal product along with sodium thiosulphate. W. A. D.

Formation of Organic Tri- and Tetra-sulphides. By J. J. Blanksma (*Rec. Trav. Chim.*, 1901, **20**, 144—145. Compare this vol., i, 264).—2 : 2′-*Dinitrodiphenyl trisulphide*, obtained by boiling *o*-dinitrobenzene (2 mols.) with alcoholic sodium trisulphide, made by dissolving sodium disulphide (1 mol.) and sulphur (1 atom) in alcohol, crystallises from alcohol in yellow, silky needles and melts at 185°. Using sodium tetrasulphide (sodium disulphide + 2 atoms of sulphur), *di*-o-*nitrophenyl tetrasulphide* is obtained in yellow needles, which crystallise from alcohol and melt at 160°; the same tetrasulphide is formed by the action of iodine on *sodium nitrodithiophenoxide*, which is present in a cold alcoholic solution of *o*-dinitrobenzene and sodium disulphide. W. A. D.

Aromatic Dicarbylamines. By Felix Kaufler (*Ber.*, 1901, **34**, 1577—1579. Compare Grassi-Cristaldi and Lambardi, Abstr., 1895, i, 568).—Aromatic dicarbylamines may be readily obtained by treating aromatic diamines with concentrated aqueous potassium hydroxide and excess of chloroform. By this means the carbylamine dissolves in the excess of chloroform and is protected from the decomposing action of the alkali.

p-*Phenylenedicarbylamine*, $C_6H_4(NC)_2$, crystallises in colourless needles, has an obnoxious odour, turns black at 130—140° and is partly transformed into the nitrile, a conversion which takes place readily at 230—260°. The *tetrabromide* melts at 137—138°. m-*Phenylenedicarbylamine* crystallises in colourless needles, turns to a brownish-black amorphous mass on exposure to the air, blackens at 75°, and gives off a gas at 90—95°. J. J. S.

Constitution of Acylhalogenalkylamides. By Julius Stieglitz and E. E. Slosson (*Ber.*, 1901, **34**, 1613—1616. Compare Norton and Tcherniac, Abstr., 1878, 971; Armstrong, Trans., 1900, **77**, 1047; Chattaway, *ibid.*, 1899, **75**, 1046; Comstock, Abstr., 1890, 1414).—Acetylchloroaniline is reduced by the action of potassium cyanide to acetanilide and thus does not react similarly to dialkylchloroamines, R_2NCl, or chloropiperidine, in which the halogen becomes replaced by cyanogen. Zinc alkyl compounds also reduce the N-chloroanilides and do not alkylate them as in the case of dichloroethylamine (Tcherniac, this Journ., 1876, i, 903).

Benzoylchloroamide and diazomethane yield the O-ether, methyl chloroiminobenzoate (Abstr., 1897, i, 43).

Acetylchloroamylamine, which is formed when acetylamylamine is treated with hypochlorous acid, may also be obtained by the acetylation of chloroamylamine, and must therefore have the constitution $C_5H_{11}\cdot NClAc$. Comstock's formulæ must be rejected. J. J. S.

Oxidation of Nitrous Acid and Nitrosoamines. By Daniel Vorländer (and, in part, Rudolf von Schilling and M. Schrödter) (*Ber.*, 1901, **34**, 1642—1646. Compare this vol., i, 444).—Nitrites differ from nitrous acid in their stability towards potassium permanganate. There is no such difference between sulphurous acid and normal sulphites. The latter are partly hydrolysed in solution and contain acid sulphite. In nitrous and sulphurous acids and the acid sulphites, there is a hydrogen atom in position 3 relatively to the unsaturated linking, for example, $H{\cdot}O{\cdot}\ddot{N}{:}O$, and $HO{\cdot}\ddot{S}{:}O{\cdot}ONa$ (compare *loc. cit.*). For the same reason, the nitroso-derivatives of secondary aromatic amines are not oxidised to nitroamines by alkaline potassium permanganate, but to nitrosoalkylaminobenzoic acids. Thus, nitrosomethyl-*o*-toluidine can be oxidised to nitrosomethylanthranilic acid; and nitrosoethyl-*o*-toluidine and nitrosoethyl-*m*-toluidine can be oxidised respectively to nitrosoethylanthranilic and nitrosoethyl-*m*-aminobenzoic acids (m. p. 133—135°).

Ethyl o-*methylaminobenzoate* melts at 39°, and boils at 172—175° under 45 mm. pressure. *Methyl* o-*ethylaminobenzoate* is a pleasant smelling oil boiling at 148—150° under 45 mm. pressure. *Nitroso*-o-*tolylglycine,* prepared from *o*-tolylglycine, melts at 44—45°, and is oxidised to *nitrosophenylglycine*-o-*carboxylic acid*, which forms a colourless, crystalline precipitate melting and decomposing at 120°.

K. J. P. O.

Oxidation of Arylaminodiacetic Acids. By DANIEL VORLÄNDER and ERICH MUMME (*Ber.*, 1901, **34**, 1647—1649).—Anilino- and *o*-toluidino-diacetic acids can both be easily titrated as dibasic acids, and give colour reactions with ferric chloride and thus contrast with anildiacetic-*o*-carboxylic acid (this vol., i, 83). The *hydrochloride* of anilinodiacetic acid, prepared by the action of hydrogen chloride on a solution of the acid in acetone, is decomposed by water. As was to be expected (compare preceding abstract and this vol., i, 454), oxidation with alkaline potassium permanganate at the ordinary temperature converts these acids very readily into oxalic acid and formylphenylglycine and *formyl*-o-*tolylglycine* respectively; the latter crystallises in prisms from water, and melts at 113—114°. K. J. P. O.

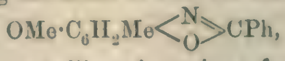
Action of Nitrous Acid on *o*-Toluidinodiacetic Acid. By DANIEL VORLÄNDER and RUDOLF VON SCHILLING (*Ber.*, 1901, **34**, 1649—1651).—*o*-Toluidinodiacetic acid is converted by nitrous acid into nitroso-*o*-tolylglycine, formaldehyde, and carbon dioxide. Glyoxylic acid is not an intermediate product in the formation of formaldehyde by the oxidation, as nitrous acid does not convert glyoxylic acid into the aldehyde.

The glyoxylic acid *compound*, with dimethylhydroresorcinol, $C_{18}H_{24}O_6$, forms needles melting at 210—212°, which contain water; the anhydrous compound melts at 230°. K. J. P. O.

Action of Hydrogen Chloride on Nitroso-*o*-tolylglycine. By DANIEL VORLÄNDER and M. SCHRÖDTER (*Ber.*, 1901, **34**, 1651—1653).—By the action of dry hydrogen chloride on alcoholic, ethereal, or acetic acid solutions of nitroso-*o*-tolylglycine, the *hydrochloride* of a chlorotolylene-*p*-diamine, $C_7H_9N_2Cl,2HCl$, is obtained as colourless crystals. The *sulphate*, $C_7H_9N_2Cl,H_2SO_4$, forms white, insoluble crystals; the *base*, $C_6H_2MeCl(NH_2)_2$, crystallises in white scales melting at 146°; the *diacetyl* derivative in white needles melting above 300°. The base is very readily oxidised to a chlorotoluquinone melting at 102° (compare Schniter, Abstr., 1887, 1036), which yields a quinol melting at 175°. K. J. P. O.

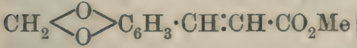
9-Aminophenanthrene. By JULIUS SCHMIDT and MAX STROBEL (*Ber.*, 1901, **34**, 1461—1467. Compare this vol., i, 76).—9-Aminophenanthrene, $C_{14}H_{11}N$, prepared by reducing 9-nitrophenanthrene (*loc. cit.*) with tin and hydrochloric acid, melts at 135—136° [Japp and Findlay give 139°], and sublimes without decomposition; it is identical with an aminophenanthrene which Pschorr (unpublished results) has prepared from 9-phenanthrenecarboxylic acid, but differs from J. A. Schmidt's liquid product (Abstr., 1879, 941). The hydrochloride forms silvery white prisms, is only very slightly soluble in water, from which it separates in needles and melts at 275°, with liberation of gas. The *picrate* separates slowly from an alcoholic solution in the form of green needles, becomes yellow at about 125°, darkens at about 180°, and melts, with liberation of gas, at 190°; from hot alcoholic or aqueous solution, it separates in yellow needles. The *acetyl* derivative crystallises from alcohol in small, white needles, sinters at 205°, and melts at 207—208° to a brown liquid. The *benzoyl* derivative crystallises from alcohol in white, silky needles, melts sharply at 199° to a clear liquid, and is the most suitable derivative for identifying the base. 9-*Phenanthrylurethane*, $C_{14}H_9{\cdot}NH{\cdot}CO_2Et$, crystallises from alcohol in glistening, white needles and melts at 156—158°. *Benzylideneaminophenanthrene*, $C_{14}H_9{\cdot}N{:}CHPh$, crystallises from alcohol in yellow prisms and melts at 108—109° to a yellow liquid. s-*Phenanthrylphenylcarbamide*, $C_{14}H_9{\cdot}NH{\cdot}CO{\cdot}NHPh$, is insoluble in most solvents, but can be purified by boiling with alcohol, sinters at 260°, and melts, with liberation of gas, at 290°. s-*Phenanthrylphenylthiocarbamide*, $C_{14}H_9{\cdot}NH{\cdot}CS{\cdot}NHPh$, separates from benzene in small, white crystals, is very slightly soluble in most solvents, and melts at 194—195° to a pale yellow liquid. T. M. L.

NOTE.—No reference is made to the earlier preparation of 9-aminophenanthrene (β-phenanthrylamine) by Japp and Findlay (Trans., 1897, **71**, 1123) by the action of ammonia on phenanthrone. EDITORS.

Constitution of Mononitrosoorcinol. By FERDINAND HENRICH (*Monatsh.*, 1901, **22**, 232—252. Compare Abstr., 1897, i, 446, and 1900, i, 163).— On treating orcinol with methyl iodide and sodium ethoxide in alcoholic solution, a mixture of methyl derivatives is formed, from which the monomethyl ether can be isolated by fractional distillation. A fraction of higher boiling point contains a substance which with nitrous acid yields a nitroso-derivative insoluble in benzene, and forming yellow needles melting at 160—165°. The aminophenol obtained by reducing the monomethyl ether of nitrosoorcinol yields a *benzoyl* derivative, $NHBz{\cdot}C_6H_2Me(OMe){\cdot}OH$, which crystallises in long needles melting at 216—218°. On heating the latter at 230° for many hours, *methoxy*-1-*phenylmethylbenzoxazole*,  $OMe{\cdot}C_6H_2Me\Big<\genfrac{}{}{0pt}{}{N}{O}\Big>CPh$, is obtained with elimination of H_2O. It crystallises in prisms from alcohol and melts at 96—97·5°. The substance was synthesised from hydroxy-1-phenylmethylbenzoxazole.

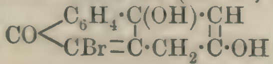
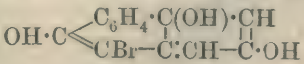
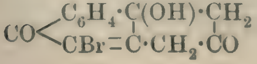
Nitroso-orcinol ethyl ether, $OEt{\cdot}C_6H_2MeO{:}NOH$, prepared from nitroso-orcinol by the action of alcoholic hydrogen chloride, crystallises in dark red prisms from alcohol and melts at 113—114°. This substance was also prepared by the action of nitrous acid on orcinol ethyl ether. K. J. P. O.

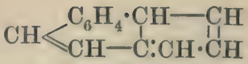
Synthetical application of Mercury Fulminate. Synthesis of Phenol Aldoximes. By ROLAND SCHOLL and ERNST BERTSCH (*Ber.*, 1901, **34**, 1441—1446).—The following method for preparing the aldoximes of polyhydric phenols is applicable in all cases in which there are two hydroxyl groups in the meta-position to one another and a free para-position. Mercury fulminate is suspended in an ethereal solution of the phenol and hydrogen chloride passed into the liquid, which must be kept cool. The method has been applied to the preparation of β-resorcyl-, orcyl-, phloroglucyl- and pyrogallol-aldoximes. The last-named compound melts at 161—162°, whilst Gattermann (Abstr., 1898, i, 581) gave 157—158° for the compound $C_6H_2(OH)_3\cdot CHO\,[OH:OH:OH:CHO = 1:2:3:4]$. T. H. P.

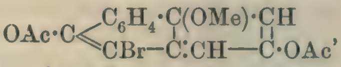
Synthesis of Acetylpiperone. By W. FEUERSTEIN and M. HEIMANN (*Ber.*, 1901, **34**, 1468—1472).—*Methyl piperonylacrylate*,  $CH_2{<}\begin{smallmatrix}O\\O\end{smallmatrix}{>}C_6H_3\cdot CH{:}CH\cdot CO_2Me$ $[CH:O_2 = 1:3:4]$, crystallises from dilute methyl alcohol in large tablets and melts at 68—69°. The *ethyl* ester forms long needles and melts at 67—68°. The *dibromide* of piperonylacrylic acid, $CH_2O_2{:}C_6H_3\cdot CHBr\cdot CHBr\cdot CO_2H$, crystallises from chloroform and melts at 143—144° with liberation of gas. *Methylenedioxybromostyrene*, $CH_2O_2{:}C_6H_3\cdot CH{:}CHBr$, prepared from the preceding compound, crystallises from dilute methyl alcohol in white needles and melts at 59°. *Piperonylacetylene*, $CH_2O_2{:}C_6H_3\cdot C{:}CH$, prepared by heating the preceding compound with potassium hydroxide, was not isolated but was converted directly into the yellow *silver* derivative; the latter was heated with alcohol and hydrochloric acid and converted directly into acetylpiperone,

$$CH_2O_2{:}C_6H_3\cdot CO\cdot CH_3,$$

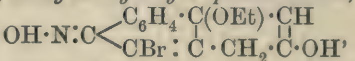
which was found to be identical with Jobst and Hesse's '*p*-coumarhydrin' (Abstr., 1880, 325), thus confirming the conclusions of Ciamician and Silber (Abstr., 1892, 873) as to the nature of the latter substance. *o-Hydroxybenzylideneacetylpiperone*, $CH_2O_2{:}C_6H_3\cdot CO\cdot CH{:}CH\cdot C_6H_4\cdot OH$, prepared by the action of sodium hydroxide on an alcoholic solution of acetylpiperone and salicylaldehyde, crystallises from alcohol in yellow needles and melts at 162—163°. T. M. L.

The Fluorescent Substance derived from Ethyl 2-Bromo-α-naphthaquinone-3-acetoacetate. By CARL T. LIEBERMANN and THEODOR LANSER (*Ber.*, 1901, **34**, 1543—1553).—The fluorescent substance formed by the action of alcoholic potash on ethyl bromonaphthaquinoneacetoacetate (Abstr., 1900, i, 311), has apparently the constitution  $CO{<}\begin{array}{l}C_6H_4\cdot C(OH)\cdot CH\\ CBr{=}C\cdot CH_2\cdot C\cdot OH\end{array}$ (I), but its properties are also in accord with the isodynamic formulæ,  $OH\cdot C{<}\begin{array}{l}C_6H_4\cdot C(OH)\cdot CH\\ CBr{-}C{:}CH{-}C\cdot OH\end{array}$ (II) and  $CO{<}\begin{array}{l}C_6H_4\cdot C(OH)\cdot CH_2\\ CBr{=}C\cdot CH_2\cdot CO\end{array}$ (III). To the parent hydrocarbon nucleus

$C_{13}H_{10}$,  $CH<\begin{array}{l}C_6H_4\cdot CH—CH\\ CH—C:CH\cdot CH\end{array}$, the name *pentanthrene* is given. The fluorescence is attributed to the hydroxyl group attached to the tertiary carbon atom present, owing to the fact that when this radicle is etherified (*loc. cit.*) or replaced by halogens (*infra*), derivatives are obtained which are not fluorescent.

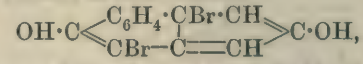
Bromodiacetoxymethoxypentanthrene,  $OAc\cdot C<\begin{array}{l}C_6H_4\cdot C(OMe)\cdot CH\\ CBr—C:CH—C\cdot OAc\end{array}$, obtained by acetylating the methyl ether of the fluorescent substance, crystallises from benzene in colourless leaflets and melts at 189—191°. The fluorescent substance itself yields with acetic anhydride at 55—60° the *compound*, $C_{28}H_{19}O_7Br$, formed by the acetylation of 1 mol. of the form III and elimination of hydrogen bromide (1 mol.) between the bromine atom of the product and the hydroxyl group of the same form.

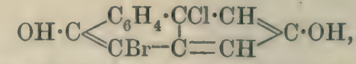
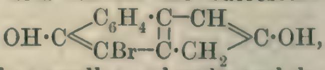
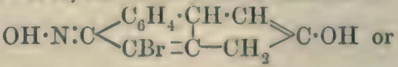
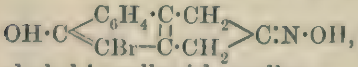
Bromoketoximohydroxyethoxydihydropentanthrene,



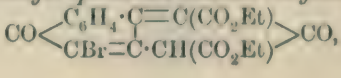
$$OH\cdot N:C<\begin{array}{l}C_6H_4\cdot C(OEt)\cdot CH\\ CBr:C\cdot CH_2\cdot C\cdot OH\end{array},$$

is obtained by the action of hydroxylamine hydrochloride on either the ethyl ether of the fluorescent substance, or the latter itself dissolved in alcohol, when etherification spontaneously occurs; it crystallises from alcohol in yellow needles and is soluble in cold alkalis.

Dibromodihydroxypentanthrene,  $OH\cdot C<\begin{array}{l}C_6H_4\cdot CBr\cdot CH\\ CBr—C═CH\end{array}>C\cdot OH$, formed at the ordinary temperature on adding hydrobromic acid of sp. gr. 1·49 to a solution of the fluorescent substance in glacial acetic acid, crystallises from dilute alcohol in colourless leaflets and melts and decomposes at 174°.

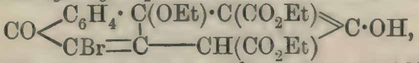
Chlorobromodihydroxypentanthrene,  $OH\cdot C<\begin{array}{l}C_6H_4\cdot CCl\cdot CH\\ CBr—C═CH\end{array}>C\cdot OH$, obtained similarly, using hydrochloric acid, melts and decomposes at 173—174°, and when mixed with aqueous potassium iodide in alcoholic solution yields the analogous *bromoiododihydroxypentanthrene* melting at 119° with decomposition. Hydriodic acid reduces the fluorescent substance to *bromodihydroxypentanthrene*,  $OH\cdot C<\begin{array}{l}C_6H_4\cdot C—CH\\ CBr—C\cdot CH_2\end{array}>C\cdot OH$, which crystallises from alcohol in colourless needles and melts and decomposes at 192°; it is also formed by reduction with zinc dust in alcoholic or glacial acetic acid solution, and, on acetylation, yields *bromodiacetoxypentanthrene*, which crystallises from alcohol and melts at 159°. With hydroxylamine, however, its behaviour is that of its tautomeric form, and the *oxime*,  $OH\cdot N:C<\begin{array}{l}C_6H_4\cdot CH\cdot CH\\ CBr═C—CH_2\end{array}>C\cdot OH$ or  $OH\cdot C<\begin{array}{l}C_6H_4\cdot C\cdot CH_2\\ CBr—C\cdot CH_2\end{array}>C:N\cdot OH$, is obtained; it crystallises from alcohol in yellowish needles.

Ethyl bromodiketodihydropentanthrenedicarboxylate,



$$CO<\begin{array}{l}C_6H_4\cdot C═C(CO_2Et)\\ CBr═C\cdot CH(CO_2Et)\end{array}>CO,$$

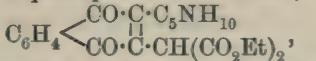
obtained by the action of 3 : 4-dibromo-β-naphthaquinone on diethyl acetonedicarboxylate (compare Michel, Abstr., 1900, i, 669), crystallises from alcohol in small, yellowish needles, melts at 157°, and is not fluorescent in alkaline solution; it is also not acted on by alcohol and sulphuric acid, or by hydrochloric or hydrobromic acids, but combines additively with alcohol in presence of sodium ethoxide to form *ethyl bromoketohydroxyethoxydihydropentanthrenedicarboxylate*,



$$\mathrm{CO}<\begin{array}{l}\mathrm{C_6H_4\cdot C(OEt)\cdot C(CO_2Et)}\\ \mathrm{CBr{=}C{-\!\!-\!\!-}CH(CO_2Et)}\end{array}>\mathrm{C\cdot OH},$$

which crystallises from alcohol in needles, melts at 135—137°, and is not fluorescent. Using *iso*butyl alcohol, the analogous iso*butyl* derivative, $C_{23}H_{25}O_7Br$, is formed; it crystallises from dilute acetic acid and melts at 142—144°.

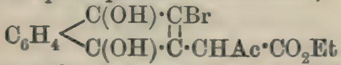
Ethyl 2-piperidino-α-naphthaquinone-3-malonate,



$$\mathrm{C_6H_4}<\begin{array}{l}\mathrm{CO\cdot C\cdot C_5NH_{10}}\\ \mathrm{CO\cdot C\cdot CH(CO_2Et)_2}\end{array},$$

prepared by the interaction of 2-bromo-α-naphthaquinone-3-malonate with piperidine in alcoholic solution, crystallises from alcohol, on adding water, in red needles and melts at 99°.

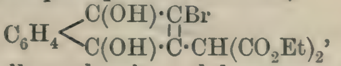
Ethyl 2-bromo-1 : 4-naphthaquinol-3-acetoacetate,



$$\mathrm{C_6H_4}<\begin{array}{l}\mathrm{C(OH)\cdot CBr}\\ \mathrm{C(OH)\cdot C\cdot CHAc\cdot CO_2Et}\end{array},$$

prepared by reducing the corresponding naphthaquinone derivative with zinc dust in glacial acetic acid solution, forms colourless crystals and melts and decomposes at 125°.

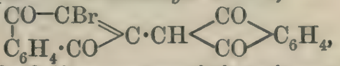
Ethyl 2-bromo-1 : 4-naphthaquinol-3-malonate,



$$\mathrm{C_6H_4}<\begin{array}{l}\mathrm{C(OH)\cdot CBr}\\ \mathrm{C(OH)\cdot C\cdot CH(CO_2Et)_2}\end{array},$$

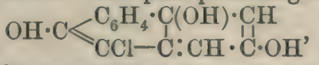
forms colourless needles and melts and decomposes at 130°.

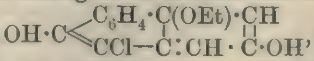
2-Bromo-α-naphthaquinone-3-diketohydrindene,



$$\begin{array}{l}\mathrm{CO{-}CBr}\\ \mathrm{C_6H_4\cdot CO}\end{array}>\mathrm{C\cdot CH}<\begin{array}{l}\mathrm{CO}\\ \mathrm{CO}\end{array}>\mathrm{C_6H_4},$$

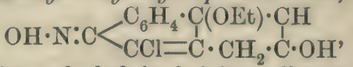
obtained by heating 2 : 3-dibromo-α-naphthaquinone with ethyl sodiodiketohydrindenecarboxylate in alcoholic solution at 150°, forms yellow needles and melts at 278°. W. A. D.

The Fluorescent Compound derived from Ethyl 2-Chloro-α-naphthaquinone-3-acetoacetate. By ALFRED BERTHEIM (*Ber.*, 1901, **34**, 1554—1558. Compare preceding abstract).—*Chlorotrihydroxypentanthrene*,  $\mathrm{OH\cdot C}<\begin{array}{l}\mathrm{C_6H_4\cdot C(OH)\cdot CH}\\ \mathrm{CCl{-}C{:}CH\cdot C\cdot OH}\end{array}$, obtained by the action of alkali on 2-chloro-α-naphthaquinone-3-acetoacetate (Michel, Abstr., 1900, i, 669), forms yellow leaflets, melts and decomposes at 140°, and is strongly fluorescent in alkaline solution; the following compounds were prepared in the same way as the analogous bromo-derivatives.

Chlorodihydroxyethoxypentanthrene,  $\mathrm{OH\cdot C}<\begin{array}{l}\mathrm{C_6H_4\cdot C(OEt)\cdot CH}\\ \mathrm{CCl{-}C{:}CH\cdot C\cdot OH}\end{array}$, crystallises from benzene in amber-yellow plates and melts at 175—176°;

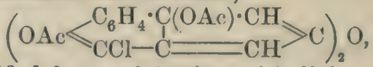
chlorodihydroxymethoxypentanthrene separates from benzene as a yellow, crystalline powder and melts at 162—164°; the analogous iso*butyl ether* forms leaflets and melts at 140—141°. *Chlorodiacetoxyethoxypentanthrene* crystallises from alcohol in small, amber coloured plates and melts at 152—153·5°; *chlorodiacetoxybutoxypentanthrene* separates from dilute acetone as a white, crystalline powder and melts at 149°.

Chloroketoximohydroxyethoxydihydropentanthrene,



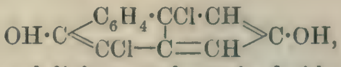
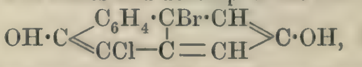
$$OH\cdot N{:}C<\begin{matrix}C_6H_4\cdot C(OEt)\cdot CH \\ CCl{=}C\cdot CH_2\cdot C\cdot OH\end{matrix}$$

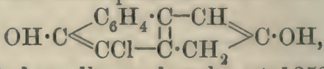
crystallises from dilute alcohol in bright yellow needles which, when heated, decompose before melting. Acetic anhydride at 55° converts the fluorescent substance into the *ether*,



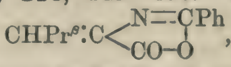
$$\left(OAc<\begin{matrix}C_6H_4\cdot C(OAc)\cdot CH \\ CCl{-}C{=\!=\!=}CH\end{matrix}>C\right)_2 O,$$

which can be purified by precipitation with light petroleum from its benzene or chloroform solution.

Dichlorodihydroxypentanthrene,  $OH\cdot C<\begin{matrix}C_6H_4\cdot CCl\cdot CH \\ CCl{-}C{=}CH\end{matrix}>C\cdot OH$, crystallises from a mixture of benzene and light petroleum in feebly yellow needles and melts and decomposes at 180°. *Chlorobromodihydroxypentanthrene*,  $OH\cdot C<\begin{matrix}C_6H_4\cdot CBr\cdot CH \\ CCl{-}C{=}CH\end{matrix}>C\cdot OH$, forms lustrous, yellow needles from benzene and melts and decomposes at 168—170°.

Chlorodihydroxypentanthrene,  $OH\cdot C<\begin{matrix}C_6H_4\cdot C{-}CH \\ CCl{-}C\cdot CH_2\end{matrix}>C\cdot OH$, crystallises from alcohol in white, felted needles and melts at 185°; its *diacetyl* derivative forms white needles and melts at 152—156°.

W. A. D.

Synthesis of *r*-Leucine. By EMIL ERLENMEYER, jun., and JULIUS KUNLIN (*Annalen*, 1901, **316**, 145—156. Compare Abstr., 1899, i, 761).—The *anhydride*,  $CHPr^{\beta}{:}C<\begin{matrix}N{=}CPh \\ CO{-}O\end{matrix}$, of α-benzoylamino-β-*iso*propylacrylic acid, prepared by heating on the water-bath a mixture of mol. proportions of hippuric acid, *iso*butaldehyde, and fused sodium acetate in the presence of acetic anhydride, crystallises from alcohol in colourless needles or plates and melts at 87°; the substance is insoluble in water but dissolves in the ordinary organic solvents. The *acid*, $CHPr^{\beta}{:}C(NH\cdot COPh)\cdot CO_2H$, obtained by treating the anhydride successively with sodium hydroxide and hydrochloric acid, crystallises from dilute alcohol in needles melting at 187°. The *silver* salt, $C_{13}H_{14}O_3NAg$, is obtained as a white precipitate; the *barium* and *calcium* salts crystallise in colourless needles. When heated with excess of concentrated ammonia solution in sealed tubes at 150—170°, the preceding acid undergoes hydrolysis, yielding *r*-leucine and benzoic and *iso*valeric acids, the amino-compound being identified by conversion into its copper salt and benzoyl derivative (Fischer, Abstr., 1900, i, 646).

G. T. M.

Dimethyl- and Diethyl-aminobenzoyltetrachlorobenzoic Acids and their Derivatives. By ALBIN HALLER and HERM. UMBGROVE (*Bull. Soc. Chim.*, 1901, [iii], 25, 598—603. Compare this vol., i, 276 and 324).—*Dimethylaminobenzoyltetrachlorobenzoic acid*, obtained by the action of dimethylaniline on tetrachlorophthalic anhydride in the presence of aluminium chloride, crystallises in small, yellow scales melting at 211°. The *methyl* and *ethyl* esters, yellow crystalline substances melting at 167° and 143° respectively, cannot be prepared by the ordinary method, but may be obtained by the action of sodium methoxide or ethoxide on the *acetate* or *mixed anhydride*. The latter compound is formed when dimethylaminobenzoyltetrachlorobenzoic acid is heated with dimethylaniline and acetic anhydride, a reaction which was expected to give rise to a phthalein such as is yielded by the non-chlorinated dialkylaminobenzoylbenzoic acids (this vol., i, 325). *Dimethylaminobenzyltetrachlorobenzoic acid*, obtained by reducing the corresponding benzoyl derivative with zinc and hydrochloric acid, crystallises in slender, white needles melting at 215°. *Diethylaminobenzoyltetrachlorobenzoic acid*, obtained in a similar manner to the corresponding methyl derivative, forms yellow crystals melting at 222°. The *methyl* and *ethyl* esters are yellow, crystalline compounds melting at 160° and 135° respectively, whilst the *acetate* or *mixed anhydride* crystallises in colourless scales melting at 175°. *Diethylaminobenzyltetrachlorobenzoic acid* forms white crystals melting at 148°. N. L.

Nitrilophenols. By EDMOND FIQUET (*Bull. Soc. Chim.*, 1901, [iii], 25, 591—598).—The action of cyanoacetic acid on *m*- and *p*-hydroxybenzaldehydes in presence of acetic acid results in the formation of cyano-*m*- and *p*-hydroxycinnamic acids. These acids form two series of salts, since they contain both phenolic and carboxylic hydroxyl, are oxidised to picric acid by the action of nitric acid, and lose carbon dioxide when heated under diminished pressure, with the production of *nitriles*. That from the *meta*-acid melts at 148°, whilst that from the *para*-acid is a liquid which partially decomposes on distillation. In the preparation of cyano-*o*-hydroxycinnamic acid, an ester or the sodium salt of cyanoacetic acid must be employed, otherwise an internal anhydride is formed by the interaction of the phenolic and carboxylic hydroxyls.

These nitriles, containing both phenolic hydroxyl and a cyanogen group, were prepared in large quantities for physiological investigation. Nitriles in general are toxic, and the effect of phenolic hydroxyl is usually to increase the toxicity of a compound, phenol, for example, being more toxic than benzene, and salicylic acid than benzoic acid. Nevertheless, the toxicity of nitriles is found to disappear on the introduction of phenolic hydroxyl, the cyanogen and phenol groups being apparently antagonistic as regards their physiological action. It is pointed out that proteid substances behave in many respects like complex nitriles, and that peptones may be compared with nitrilophenols, the non-toxicity of which is due to a state of physiological equilibrium. It would seem also that the introduction of phenols into the organism not only prevents the development of micro-organisms, but neutralises the toxicity of the products secreted by them. N. L.

Preparation of the Esters of *o*-, *m*-, and *p*-Nitrobenzoylcyanoacetic Acid and Crystallised *o*-Nitrobenzoic Chloride. By MAVROJANNIS (*Compt. rend.*, 1901, 132, 1054—1055).—Substituted benzoyl derivatives of ethyl cyanoacetate are produced by treating the sodium derivative of this ester dissolved in alcohol with an ethereal solution of the corresponding acid chloride.

Ethyl o-*nitrobenzoylcyanoacetate*, $NO_2\cdot C_6H_4\cdot CO\cdot CH(CN)\cdot CO_2Et$, obtained by the use of *o*-nitrobenzoic chloride, separates from ether in prismatic crystals melting at 89°; it is almost insoluble in water but readily dissolves in the ordinary organic solvents. *o*-Nitrobenzoic chloride, when freed from phosphorus oxychloride by distillation under 50 mm. pressure, slowly solidifies and separates from its solution in light petroleum in colourless crystals melting at 24—25°.

Ethyl m-*nitrobenzoylcyanoacetate* crystallises from alcohol in silky needles and melts at 110°; its *para*-isomeride also separates in white needles melting at 158°; these esters are almost insoluble in water and dissolve but sparingly in the ordinary organic solvents.

G. T. M.

Derivatives of Anthranilic Acid. By HANS MEHNER (*J. pr. Chem.*, 1901, [ii], 63, 241—312).—By the action of formaldehyde on anthranilic acid in acid solution, a yellow, amorphous substance is obtained.

Methyl methylenedi-o-aminodibenzoate, $CH_2(NH\cdot C_6H_4\cdot CO_2Me)_2$, formed when formaldehyde condenses with methyl *o*-aminobenzoate without a condensing agent, crystallises in needles melting at 119—120° and boils and partially decomposes at 280°; its solution exhibits an intense blue fluorescence. On heating with ammonia, it yields hexamethylenetetramine; by acids, it is decomposed into formaldehyde and methyl *o*-aminobenzoate.

Methyl-4 : 4′-*diaminodiphenylmethane*-3 : 3′-*dicarboxylate*,

$$CH_2[C_6H_3(NH_2)\cdot CO_2Me]_2,$$

produced by isomeric change from the last-mentioned compound by warming with hydrochloric acid, crystallises in white plates melting at 147°, and forms a *dihydrochloride*, a *diacetyl* derivative, which crystallises in lustrous plates melting at 161—163°, and a *dibenzoyl* derivative forming needles which melt at 221·5°.

On treating the diazonium derivative of the base with aniline hydrochloride, a mixture of a mono- and a di-diazoamino-compound is obtained. The *oxyazo*-derivative of the base and *β*-naphthol, $CH_2[C_6H_3(CO_2Me)\cdot N_2H{:}C_{10}H_6O]_2$, forms small, dark-red crystals; the *compound* with phenol, $CH_2[C_6H_3(CO_2Me)\cdot N_2\cdot C_6H_4\cdot OH]_2$, was obtained as a dark-red powder.

4 : 4′-*Diaminodiphenylmethane*-3 : 3′-*dicarboxylic acid*, prepared from the ester, forms yellowish needles which melt at 239°; the salts are all unstable. The *monomethyl* ester is produced by boiling methyl methylenediaminodibenzoate with hydrochloric acid for 1 hour, when

isomerisation and partial hydrolysis take place, crystallises in needles melting at 178—179°, and forms a *silver* salt, $C_{16}H_{15}O_4N_2Ag$.

Methyl ethylidenedi-o-aminodibenzoate, $CHMe(NH\cdot C_6H_4\cdot CO_2Me)_2$, prepared by the action of acetaldehyde on methyl *o*-aminobenzoate in ethereal solution, crystallises in large, colourless crystals melting at 130—131°; in solution, it exhibits a blue fluorescence, and is decomposed by acids. Transformation into a diphenylethane could not be effected. Attempts to benzoylate it led to the production of *methyl o-benzoylaminobenzoate*, $NHBz\cdot C_6H_4\cdot CO_2Me$, which crystallises in needles melting at 100°. In acid solution, acetaldehyde forms with methyl *o*-aminobenzoate a *derivative* of aldol,

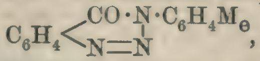
$$CO_2Me\cdot C_6H_4\cdot NH\cdot CHMe\cdot CH_2\cdot CH\dot{:}N\cdot C_6H_4\cdot CO_2Me,$$

which forms colourless crystals melting at 146°.

Derivatives of methyl diazoaminobenzene-2-carboxylate. Methyl o-diazoaminobenzoate, $N_3HPh\cdot C_6H_4\cdot CO_2Me$, prepared by adding aniline hydrochloride to diazotised methyl *o*-aminobenzoate, crystallises in yellow needles melting at 71°. The same diazoamino-compound is obtained when benzenediazonium nitrate and the methyl ester interact in pyridine, but not in aqueous, solution. Attempts to transform this compound into the azoamino-compound failed. 3-Phenylphenotriazone and methyl alcohol are formed when the last-mentioned diazoamino-compound is boiled with dilute alcohol; the former is identical with the substance obtained by Pictet and Gonset (Abstr., 1898, i, 213). Heated with concentrated hydrochloric acid, the triazone yields chiefly *o*-chlorobenzoic acid. Reduction with stannous chloride produces anthranilic acid and phenylhydrazine. Alcoholic sodium hydroxide converts it into *sodium o-diazoaminobenzoate*, which crystallises in sulphur-yellow needles.

o-Diazoaminobenzoic acid, $N_3HPh\cdot C_6H_4\cdot CO_2H$, prepared from the sodium salt, or from anthranilic acid and benzenediazonium chloride, forms unstable, faintly yellow leaves or prisms, melting and decomposing at 121°. The *potassium*, *ammonium*, and *silver* salts are all sparingly soluble in water.

Methyl o-toluenediazoaminobenzoate, $C_6H_4Me\cdot N_3H\cdot C_6H_4\cdot CO_2Me$, prepared from *o*-toluidine hydrochloride and diazotised methyl *o*-aminobenzoate, crystallises in yellow needles melting at 69·5°. The corresponding *para*-compound forms straw-yellow needles melting at 115·5°, and the *meta*-compound together with *methyl m-toluidineazobenzoate*, $NH_2\cdot C_6H_2Me\cdot N_2\cdot C_6H_4\cdot CO_2Me$, are formed from *m*-toluidine hydrochloride and diazotised methyl *o*-aminobenzoate. The diazoamino-derivative crystallises in yellow needles melting at 87·5°; the azoamino-compound separates in red needles melting at 93°, and is far less soluble in petroleum than the diazoamino-compound.

3-o-Tolylphenotriazone,  $C_6H_4{<}{\begin{matrix}CO\cdot N\cdot C_6H_4Me\\ N{=}\overset{|}{N}\end{matrix}}$, obtained from the corresponding diazoamino-compound, forms small, colourless needles melting at 166°. 3-p-*Tolylphenotriazone* crystallises in small needles or prisms melting at 143°, and 3-m-*tolylphenotriazone* in needles melting at 150°. These three substances are obtainable respectively from the three *o*-aminobenzoyltoluidides.

Methyl m-xylenediazoaminobenzoate, $C_6H_3Me_2\cdot N_3H\cdot C_6H_4\cdot CO_2Me$, crystallises in yellow needles melting at 85°. 3-m-*Xylylphenotriazone*, prepared from the latter, crystallises in white needles melting at 132°.

o-*Aminobenzoyl-o-toluidide*, $NH_2\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4Me$, prepared by heating isatoic anhydride with *o*-toluidine (compare Kolbe, Abstr., 1885, 58), crystallises in white needles melting at 104°. The p-*toluidide* forms needles melting at 151°, the m-*toluidide* needles melting at 118°, and the m-*xylidide* needles melting at 138°. By the action of sodium nitrite in acid solution, these compounds are converted into the triazones already described.

Methyl m-*nitro*-o-*diazoaminobenzoate*, prepared from *m*-nitroaniline and methyl *o*-diazobenzoate, forms yellow needles melting at 167°. 3-m-*Nitrophenylphenotriazone* crystallises in white needles melting at 238°. *Methyl* p-*nitro*-o-*diazoaminobenzoate* crystallises in golden-yellow needles melting at 184°, and is converted into 3-p-*nitrophenylphenotriazone*, which crystallises in colourless needles melting at 252—254°. Both these nitro-esters are converted with ease into the triazones, and in this respect contrast with the corresponding methyl derivatives previously described. In no circumstances could a condensation be effected between *o*-nitroaniline and methyl *o*-diazobenzoate.

Monomethyl diazoaminobenzene-2 : 2′-*dicarboxylate*,

$$CO_2Me\cdot C_6H_4\cdot N_2H\cdot C_6H_4\cdot CO_2H,$$

prepared from methyl *o*-diazobenzoate and anthranilic acid, crystallises in small needles, which melt and decompose at 127° and could not be converted into a triazone.

With *m*-phenylenediamine, methyl *o*-diazobenzoate yields the *hydrochloride* of *methyl chrysoidine-2-carboxylate*, $C_{14}H_{14}O_2N_4,HCl,H_2O$, which forms violet-red needles; the *base*, $C_6H_3(NH_2)_2\cdot N_2\cdot C_6H_4\cdot CO_2Me$, crystallises in brownish-red leaves which melt at 138°. The diazoamino-compound could not be obtained.

m-*Toluenediazoaminobenzoic acid*, $C_6H_4Me\cdot N_3H\cdot C_6H_4\cdot CO_2H$, is obtained by the action of *m*-toluenediazonium salts on anthranilic acid, and not by the action of *o*-diazobenzoic acid on *m*-toluidine except in pyridine solution; it forms pale yellow plates melting and decomposing at 114°. The p-*toluene* compound crystallises in pale yellow leaves, melting and decomposing at 118°. Neither diazotised *o*-toluidine nor *m*-xylidine could be induced to combine with anthranilic acid; the presence of the methyl group in the ortho-position appears to prevent the condensation.

o-*Nitrodiazoaminobenzene-2-carboxylic acid*,

$$NO_2\cdot C_6H_4\cdot N_3H\cdot C_6H_4\cdot CO_2H,$$

prepared from *o*-nitrobenzenediazonium salts and anthranilic acid, forms small, golden-yellow needles melting and decomposing at 140°; the m-*nitro*-derivative crystallises in pale yellow needles melting and decomposing at 166·5°, the p-*nitro*-derivative in small, yellow needles melting and decomposing at 171°. None of these acids could be converted into a triazone. They can, however, all be obtained by boiling the triazones with alcoholic sodium hydroxide or by hydrolysing the corresponding methyl esters.

o-*Toluenediazoaminobenzoic acid*, $C_6H_4Me\cdot N_3H\cdot C_6H_4\cdot CO_2H$, obtained from the triazone previously described, forms pale yellow leaflets, melting and decomposing at 95—96°.

m-*Xylenediazoaminobenzoic acid*, easily prepared from the corresponding triazone, crystallises in pale yellow leaflets melting and decomposing at 117°.

A convenient and simple apparatus for measuring the nitrogen given off from a diazoamino-compound under the action of an acid is described; it is a modification of that devised by Goldschmidt and Reinders (Abstr., 1896, ii, 515), and is found to give accurate results. By its means, the relative proportion of diazoamino- and aminoazo-derivatives, formed from methyl *o*-diazobenzoate and the hydrochlorides of various aromatic bases, have been determined. Aniline yields 92·2 per cent. of diazoamino-compound, *o*-toluidine 93·0, *m*-toluidine 64·24, *p*-toluidine 98·53, and *m*-xylidine 95·2 per cent. K. J. P. O.

Esters of Phoroglucinolcarboxylic Acids. By JOSEF HERZIG and FRANZ WENZEL [and, in part, PAUL ALTMANN] (*Monatsh.*, 1901, **22**, 215—231. Compare Abstr., 1900, i, 176).—The method of preparing methyl phloroglucinolcarboxylate previously given (*loc. cit.*) from methyl iodide and silver phloroglucinolcarboxylate is found to yield, not only the above ester (m. p. 170—172°), but also methyl dimethylphloroglucinolcarboxylate and phloroglucinolcarboxylic acid; the quantity of the latter largely preponderates.

Methyl dimethylphloroglucinolcarboxylate, $C_6Me_2(OH)_3{\cdot}CO_2Me$, crystallises from dilute alcohol in white needles melting at 138—140°. The *monoacetate*, prepared by boiling the ester for ½ hour with acetic anhydride, melts at 98—101°; the *triacetate*, formed only in the presence of sodium acetate, melts at 124—126°.

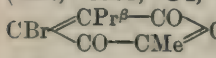
By the action of acetic anhydride on methyl phloroglucinolcarboxylate, a *diacetate* is obtained melting at 83—86°; whilst in the presence of sodium acetate the *triacetate* is formed, melting at 77—79°.

Methoxyphloroglucinolcarboxylic acid, $OMe{\cdot}C_6H_2(OH)_2{\cdot}CO_2H$, prepared as the sodium salt by heating the sodium derivative of methoxyphloroglucinol with carbon dioxide under a pressure of 5 atmospheres, crystallises in grey needles melting and decomposing at 141°.

Methyl methoxyphloroglucinolcarboxylate cannot be prepared by the usual methods, but is readily obtained by treating the acid in ethereal solution with diazomethane. It forms colourless needles, melting at 114—116°. With alcoholic potash, the ester yields only methoxyphloroglucinol. It is, however, easily converted into the acid by heating with concentrated sulphuric acid at 90—95° for 10 minutes.

K. J. P. O.

Some Derivatives of Dibromothymoquinone. By J. HOFFMANN (*Ber.*, 1901, **34**, 1558—1561).—*Ethyl bromothymoquinonemalonate*,



$\mathrm{CBr}{<}\genfrac{}{}{0pt}{}{\mathrm{CPr^{\beta}{—}CO}}{\mathrm{CO{—}CMe}}{>}\mathrm{C{\cdot}CH(CO_2Et)_2}$, obtained by the action of ethyl sodiomalonate on dibromothymoquinone suspended in alcohol, crystallises in yellow needles and melts at 78°; the *barium* salt is an amorphous blue powder. The action of either ethyl cyanoacetate or ethyl acetoacetate on dibromothymoquinone yields only oily products.

When *p*-toluidine is boiled with dibromothymoquinone in alcoholic solution, a methyl group, not a bromine atom, is replaced, 2-p-*toluidino*-

3 : 6-*dibromo*-5-iso*propyl*-1 : 4-*benzoquinone* being formed; it crystallises from alcohol in dark violet needles and melts at 195°. 3 : 6-*Dibromo-2-anilino*-5-iso*propyl*-1 : 4-*benzoquinone*, obtained by using aniline, crystallises from alcohol in dark blue needles and melts at 170°; Carstanjen (this Journal, 1871, 350) has stated, without analysing his product, that this action yields a dianilinothymoquinone. The structure of the anilide and toluidide follows from their both yielding 3 : 6-*dibromo-2-hydroxy*-5-iso*propyl*-1 : 4-*benzoquinone* when boiled with 20 per cent. alcoholic sulphuric acid for 2—3 hours; this crystallises from light petroleum in reddish-brown needles, melts at 143° and yields a *silver* derivative, which separates from alcohol in red needles. The latter with methyl iodide gives 3 : 5-*dibromo-2-methoxy*-5-iso*propyl*-1 : 4-*benzoquinone*, which crystallises from methyl alcohol in yellow leaflets and melts at 62—63°; the analogous *ethoxy*-derivative crystallises from ethyl alcohol in golden leaflets and melts at 59—60°. W. A. D.

Friedel and Crafts' Reaction. By J. Boeseken (*Rec. Trav. Chim.*, 1901, **20**, 102—106).—In support of views previously stated (Abstr., 1900, i, 349; compare Perrier, *ibid.*, 331), it is shown that acetyl chloride combines with aluminium chloride in carbon disulphide solution at $-10°$, giving the *additive* compound, $AcCl,AlCl_3$; it is a non-crystallisable, yellowish syrup, which interacts with benzene in carbon disulphide solution to form the *compound*, $COPhMe,AlCl_3$, melting at 64°. This, when decomposed by water, yields acetophenone; in like manner, acetyltoluene and acetylxylene were prepared.

Contrary to Combe's statement (*Ann. Chim. Phys.*, 1887, [vi], **12**, 199), when the product resulting from the complete condensation of acetyl chloride with aluminium chloride to form $CH_2Ac{\cdot}CO{\cdot}CH_2{\cdot}COCl$, is boiled with benzene, no acetophenone is formed; the latter is only obtained in cases where some of the acetyl chloride has remained unacted on. W. A. D.

Disulphones. VI. Sulphonal Derivatives of Unsaturated Ketones. By Theodor Posner (*Ber.*, 1901, **34**, 1395—1405).—Substances such as mesityl oxide, $CMe_2{:}CH{\cdot}CO{\cdot}CH_3$, benzylideneacetone, $CHPh{:}CH{\cdot}CO{\cdot}CH_3$, benzylideneacetophenone, $CHPh{:}CH{\cdot}CO{\cdot}C_6H_5$, and dypnone, $CMePh{:}CH{\cdot}CO{\cdot}C_6H_5$, which contain a ketonic carbonyl group and one neighbouring double bond, condense with 3 mols. of ethyl hydrosulphide when the mixture of unsaturated ketone and hydrosulphide is saturated with dry gaseous hydrogen chloride; the grouping $C{:}CH{\cdot}CO$ becomes $CH{\cdot}CH(SEt){\cdot}C(SEt)_2$. On the other hand, when there are two double bonds adjoining the ketonic carbonyl, as in phorone, $CO(CH{:}CMe_2)_2$, and dibenzylideneacetone, $CO(CH{:}CHPh)_2$, the substance reacts with 2 mols. only of the hydrosulphide, and not with 4; only the carbonyl reacts, the grouping $CO(CH{:}C)_2$ becoming $C(SEt)_2(CH{:}C)_2$. Cold aqueous potassium permanganate oxidises these thioethyl compounds (mercaptoles) respectively to trisulphones with the grouping $CH{\cdot}CH(SO_2Et){\cdot}C(SO_2Et)_2$, or disulphones with $C(SO_2Et)_2(CH{:}C)_2$. In the case of benzylideneacetone, however, the main product of the oxidation is not a trisulphone, but a ketomonosulphone with the grouping $CH{\cdot}CH(SO_2Et){\cdot}CO$; this is less soluble in alcohol than the normal product, which is formed also, although in small amount. The trisulphones do not react with bromine, as indeed might be expected; the disulphones, however, which still contain (two) double bonds, do react slowly; hydrogen bromide is eliminated, and the product is a bromo-substitution derivative, dibromo- in the case of the phorone compound, monobromo- in the case of dibenzylideneacetone. Presumably the primary product in each case was an additive product, with 4Br and 2Br respectively.

The compounds described are enumerated below with their melting points; the thioethyl compounds (mercaptoles) were obtained as oils, and were not analysed. From mesityl oxide: *γδδ-Trithioethyl-β-methylpentane* (*mesityl oxide sesquimercaptole*); *γδδ-triethylsulpho-β-methylpentane* (*mesityl oxide trisulphone*), 100°. From phorone: *δ-Dithioethyl-βζ-dimethylhepta-βε-diene* (*phorone mercaptole*); *δ-diethylsulpho-βζ-dimethylhepta-βε-diene* (*phorone disulphone*), 101°, *dibromo*-derivative, 139—140°. From benzylideneacetone: *ββγ-Trithioethyl-δ-phenylbutane* (*benzylideneacetone sesquimercaptole*); *ββγ-triethylsulpho-δ-phenylbutane* (*benzylideneacetone trisulphone*), 154°. From dibenzylideneacetone: *γ-Dithioethylsulpho-αε-diphenylpenta-αγ-diene* (*dibenzylideneacetone mercaptole*); *γ-diethylsulphone-αε-diphenylpenta-αγ-diene* (*dibenzylideneacetone disulphone*), 140—142°, *monobromo*-derivative, 173°. From benzylideneacetophenone: *ααβ-Trithioethyl-αγ-diphenylpropane* (*benzylideneacetophenone sesquimercaptole*); *β-ethylsulpho-αγ-diphenylpropan-α-al* (*benzylideneacetophenone ketomonosulphone*), 156°; *ααβ-triethylsulpho-αγ-diphenylpropane* (*benzylideneacetophenone trisulphone*), 125°. From dypnone: *ααβ-Trithioethyl-αγ-diphenylbutane* (*dypnone sesquimercaptole*); *ααβ-Triethylsulpho-αγ-diphenylbutane* (*dypnone trisulphone*), 120—120·5°.

C. F. B.

Phenylacetylacetophenone (Phenylacetylbenzoylmethane, Phenacyl Benzyl Ketone). By Carl Bülow and Hans Grotowsky (*Ber.*, 1901, **34**, 1479—1488).—*Phenylacetylacetophenone*,

$$CH_2Ph\cdot CO\cdot CH_2\cdot COPh,$$

prepared by the action of sodium on a mixture of ethyl phenylacetate and acetophenone in the presence of ether, crystallises in colourless prisms, melts at 54—56°, and gives a red coloration with ferric chloride in alcoholic solution. The *copper* compound, $Cu(C_{16}H_{13}O_2)_2$, forms greyish-green needles which melt and decompose at 117°. No dioxime or diphenylhydrazone could be obtained, and it appears probable that after the replacement of the oxygen of one carbonyl group, the resulting keto-monoxime or monophenylhydrazone passes into the enolic form, and then loses water. 3 (or 5)-*Phenyl*-5 (or 3)-*benzylisooxazole*, $C_{16}H_{13}ON$, is formed by the action of hydroxylamine hydrochloride on the diketone and crystallises in colourless prisms melting at 92°. 1 : 3 (or 5)-*Diphenyl*-5 (or 3)-*benzylpyrazole*, $C_{22}H_{18}N_2$, is obtained by the action of phenylhydrazine on the diketone, and crystallises in fascicular groups of needles melting at 76°. The diketone also reacts with semicarbazide, forming 5 (or 3)-*phenyl*-3 (or 5)-*benzylpyrazole*, $C_{16}H_{14}N_2$, which crystallises in colourless needles melting at 90·5—91°. *Benzeneazophenylacetylacetophenone*, $COPh\cdot CH(N_2Ph)\cdot CO\cdot CH_2Ph$, is formed by the action of benzenediazonium chloride on the diketone, and crystallises in yellow, lustrous needles melting at 119—120°. When heated with a large excess of phenylhydrazine, it yields 4-*benzeneazo-1 : 3* (or 5)-*diphenyl*-5 (or 3)-*benzylpyrazole*, $C_{28}H_{22}N_4$, which crystallises in orange-red, lustrous needles melting at 150°, and can be distilled almost without decomposition. iso*Nitrosophenylacetylacetophenone*, $COPh\cdot C(:N\cdot OH)\cdot CO\cdot CH_2Ph$, formed by the action of amyl nitrite and hydrochloric acid on the diketone, crystallises in colourless needles which melt and decompose at 131°. It was found impossible to obtain a triketone by hydrolysis of this compound, dilute acids and alkalis, and even alcohol, yielding on boiling hydrogen cyanide, phenylacetic acid, and benzoic acid. iso*Nitrosophenylacetylacetophenonemonosemicarbazone*, forms colourless crystals and decomposes at about 220°. The corresponding *monoxime* crystallises in colourless prisms and melts and decomposes at 167°. A. H.

Synthesis of Luteolin. By E. DILLER and STANISLAUS VON KOSTANECKI (*Ber.*, 1901, **34**, 1449—1453).—2 : 4 : 6 : 3′ : 4′-Pentamethoxybenzoylacetophenone, $C_6H_2(OMe)_3\cdot CO\cdot CH_2\cdot CO\cdot C_6H_3(OMe)_2$ (this vol., i, 92), prepared by a slightly modified method, has been obtained in a crystalline form, separates from alcohol in small, nodular aggregates or crystalline crusts, and melts at 112—113·5°.

2 : 4 : 6 : 3′-*Tetramethoxy*-4′-*ethoxybenzoylacetophenone*,

$$C_6H_2(OMe)_3\cdot CO\cdot CH_2\cdot CO\cdot C_6H_3(OMe)\cdot OEt,$$

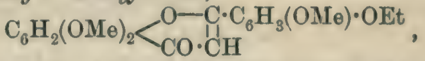
separates from alcohol in crystalline crusts consisting of minute needles and melts at 106—107°. The iso*nitroso*-derivative, $C_{21}H_{23}NO_8$, prepared by the action of amyl nitrite and hydrochloric acid on a solution in chloroform of the diketone, crystallises from a mixture of acetic acid and alcohol in short, stout, yellow needles and melts at 170° with liberation of gas.

iso*Nitroso*-2 : 4 : 6 : 4′-*tetramethoxybenzoylacetophenone*,

$$C_6H_2(OMe)_3\cdot CO.C(:NOH)\cdot CO\cdot C_6H_4\cdot OMe,$$

crystallises from a mixture of acetic acid and alcohol in yellow prisms and melts at 189° with liberation of gas.

5 : 7 : 3′-*Trimethoxy*-4′-*ethoxyflavone*,



$$C_6H_2(OMe)_2<\begin{array}{l}O{-}C\cdot C_6H_3(OMe)\cdot OEt\\ \quad\ \ \|\\ CO\cdot CH\end{array},$$

prepared by adding the tetramethoxyethoxyacetophenone to warm hydriodic acid of sp. gr. 1·7, crystallises from xylene in white needles and melts at 222—222·5° ; it is only slowly converted into luteolin by heating with hydriodic acid of sp. gr. 1·9, and the luteolin, which crystallises in needles, is mixed with a *luteolin methyl ether*, $C_{16}H_{12}O_6$, crystallising in flakes (compare Perkin and Horsfall, Trans., 1900, **77**, 1320), which melts at 270° and is probably 7-methoxy-5 : 3′ : 4′-trihydroxyflavone, for Perkin appears to have obtained it also from luteolin-7 : 3′ : 4′-trimethyl ether.

Fleischer's digitoflavone (Abstr., 1899, i, 631) very closely resembles luteolin and is perhaps identical with it. T. M. L.

Isomeric Bromodiphenacyls. By CARL PAAL and HERM. STERN (*Ber.*, 1901, **34**, 1609—1613. Compare Fritz, Abstr., 1896, i, 151 ; Paal and Demeler, *ibid.*, 687).—The two isomeric bromodiphenacyls readily form additive compounds with acid chlorides. The derivatives from the bromodiphenacyl melting at 129° are termed α- and the isomeric substances β-compounds. They are readily formed when the constituents are gently warmed together, best in sealed tubes at 100° or 110°. The following compounds are described :

	α-Bromodiphenacyl.	β-Bromodiphenacyl.
Acetyl chloride	Needles, m. p. 122°	Prisms, m. p. 91°.
Valeryl chloride	„ m. p. 146°	m. p. 101°.
Benzoyl chloride	„ m. p. 152°	Needles m. p. 134—135°.

Most of the compounds crystallise well from alcohol. J. J. S.

Constitution of Camphor. By OSSIAN ASCHAN (*Annalen*, 1901, **316**, 196—241. Compare Abstr., 1896, i, 492).—This communication, although an important contribution to the chemistry of camphor from the stereochemical standpoint, is not suitable for abstraction. The experimental results described in the paper have already been published (Abstr., 1894, i, 538). The production of inactive camphane by reducing *l*- or *d*-bornyl iodide (*l*- or *d*-pinene hydriodide) is very weighty evidence in favour of Bredt's formula for camphor (Abstr., 1894, i, 422 ; 1900, i, 399). G. T. M.

Myrcenol and its Constitution. By PHILIPPE BARBIER (*Compt. rend.*, 1901, **132**, 1048—1050).—The name *myrcenol* is given to the alcohol obtained by Power and Klèber (Abstr., 1895, ii, 295) on hydrating myrcene, the compound being isomeric and not identical with licareol. Myrcenol is a colourless, oily liquid boiling at 99—101° under 10 mm. pressure, and slowly undergoing polymerisation ; it has a sp. gr. 0·9012 at 14·5°, and n_D 1·47787 at the same temperature. The molecular refraction as deduced from experiment is 48·35, whilst the theoretical value of the latter constant calculated on the assumption of two double linkings is 48·60. *Myrcenyl acetate*, $C_{10}H_{17}O{\cdot}Ac$, is a colourless liquid boiling at 111—112°. The boiling points of the alcohol and its acetate are markedly different from the corresponding constants observed in the case of licareol. Myrcenol, when oxidised with a sulphuric acid solution of chromic acid, yields acetone, lævulic acid, and an *aldehyde*, $C_{10}H_{16}O$, boiling at 110° under 10 mm. pressure. This aldehyde is first isolated in the form of its oxime, $C_{10}H_{17}NO$, which boils at 148—150° under 10 mm. pressure ; the *semicarbazone*, $C_{10}H_{16}{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$, is a crystalline powder melting at 195—196°. When myrcenol is oxidised, first with 1 per cent. permanganate solution and then with chromic acid mixture, it yields only lævulic and succinic acids.

These results indicate that the constitution of myrcenol and myrcene may be represented by the formulæ

$$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe(OH){\cdot}CH{:}CH_2$$

and $CMe_2{:}CH{\cdot}CH_2{\cdot}CH{:}CMe{\cdot}CH{:}CH_2$ respectively. The formation of the aldehyde $C_{10}H_{16}O$ results from the oxidation of the terminal methylene group to ${:}CH{\cdot}OH$, and subsequent rearrangement comparable with that obtaining among the initial members of the olefine series when these are oxidised to the corresponding aldehydes.

G. T. M.

Dyeing with Oxidic Mordants. By CARL T. LIEBERMANN (*Ber.*, 1901, **34**, 1562—1565).—A reply to a misstatement by A. Buntrock (*Rev. gén. matières colorantes*, 1901, **5**, 99) of the author's views as to the dyeing properties of anthraquinone derivatives (Liebermann and Kostanecki, Abstr., 1885, 1209; *Annalen*, 1887, **240**, 246).

W. A. D.

Brazilin and Hæmatoxylin. Part VI. Brazilein. By JOSEF HERZIG and JACQUES POLLAK (*Monatsh.*, 1901, **22**, 207—214. Compare Abstr., 1899, i, 381, 821).—The constitutional formula to be assigned to brazilin is discussed in the light of the recent work of Gilbody and Perkin (Proc., 1899, **15**, 27, 75, 241, and 1900, **16**, 105), and the view is expressed that the constitution of brazilein offers the key to the solution of the problem.

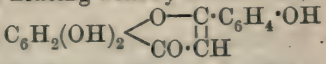
Although brazilein cannot itself be acetylated, the substance obtained from it by reduction with zinc dust and acetic acid yields a *tetra-acetyl* derivative, $C_{16}H_8(OAc)_4$, which crystallises in white plates from acetic acid, melting at 210—211°. All attempts to remove the acetyl groups failed. On hydrolysis with alkalis, a red solution is obtained, resembling alkaline solutions of brazilein. In the reduction, the fifth oxygen atom of brazilein, $C_{16}H_{12}O_5$, which is not hydroxylic, has been entirely removed, and only the four hydroxylic oxygen atoms remain.

K. J. P. O.

Preparation and composition of the Digitalis Glucosides. By MAX CLOETTA (*Chem. Centr.*, 1901, i, 1102—1103; from *Arch. exp. Path. Pharm.*, 1901, **45**, 435—446).—Crystalline and amorphous digitonin are both precipitated by adding ether to a solution of "digitalinum germanicum" in 90 per cent. alcohol, but when the mixture is dissolved in water, alcohol added, and the solution shaken with ether, crystals separate from the ethereal extract after a time, and by repeating the process, a pure crystallised digitonin, $C_{28}H_{47}O_{14}+H_2O$, may be isolated. It is easily soluble in hot water or alcohol, and with warm concentrated hydrochloric acid forms a yellow solution which quickly becomes green. Its solutions give a precipitate with tannic acid, lead acetate, and ammonia, but not with magnesium sulphate and ammonium sulphate. The anhydrous compound is prepared by adding absolute alcohol to a solution of the hydrate in 96 per cent. alcohol. The leaves of *Digitalis* also contain an extremely small quantity of crystalline digitonin.

Amorphous digitonin, $C_{27}H_{46}O_{14}$, prepared from the mother liquor of the preceding compound, is a very hygroscopic white powder, is readily soluble in water, and on warming with concentrated hydrochloric acid forms a red coloration. Unlike crystalline digitonin, the amorphous compound gives Keller's reaction, and its solutions also form a precipitate, not only with tannic acid, lead acetate, and ammonia, but also with magnesium sulphate and ammonium sulphate. Schmiedeberg's amorphous, and Kiliani's crystalline, digitonin must therefore be different compounds.

Amorphous digitonin is contained in both the leaves and seeds of *Digitalis purpurea*; digitoxin has also been found in the seeds. Attempts to isolate "digitalinum verum" from the leaves were not successful. E. W. W.

An Isomeride of Apigenin. By STANISLAUS VON KOSTANECKI and FRANZ WEBEL (*Ber.*, 1901, **34**, 1454—1457).—Ethyl *o*-ethoxybenzoate condenses with *s*-trimethoxyacetophenone in presence of metallic sodium to form 2 : 4 : 6-*trimethoxy-2'-ethoxybenzoylacetophenone*, $C_6H_2(OMe)_3\cdot CO\cdot CH_2\cdot CO\cdot C_6H_4\cdot OEt$, which crystallises from alcohol in long, striated prisms and melts at 112°. By heating with hydriodic acid, it is converted into 5 : 7 : 2'-*trihydroxyflavone*,  $C_6H_2(OH)_2<\begin{matrix}O-C\cdot C_6H_4\cdot OH\\ \quad\ \ \|\\ CO\cdot CH\end{matrix}$, which crystallises from acetic acid in pale yellow needles, and melts at 281°; the *triacetyl* derivative, $C_{21}H_{16}O_8$, crystallises from alcohol in white, silky needles and melts at 178°. 5-*Hydroxy*-7 : 2'-*dimethoxyflavone*, $C_{15}H_7O_2(OMe)_2\cdot OH$, prepared by the action of methyl iodide and potassium hydroxide on an alcoholic solution of the trihydroxyflavone, crystallises from alcohol in groups of pale yellow needles, melts at 154—156^c, and gives a sparingly soluble, yellow sodium salt; the *acetyl* derivative, $C_{15}H_7O_2(OMe)_2\cdot OAc$, crystallises from dilute alcohol in white needles and melts at 96—97°. 5-*Hydroxy*-7 : 2'-*diethoxyflavone*, $C_{15}H_7O_2(OEt)_2\cdot OH$, crystallises from alcohol in pale yellow needles and melts at 108—110°; the *acetyl* derivative, $C_{15}H_7O_2(OEt)_2\cdot OAc$, crystallises from dilute alcohol in white needles and melts at 120—122°.

5 : 7-*Dimethoxy-2'-ethoxyflavone*, $C_{15}H_7O_2(OMe)_2\cdot OEt$, prepared by cautiously heating trimethoxyethoxybenzoylacetophenone with hydriodic acid, crystallises from alcohol in white needles and melts at 164—165°. T. M. L.

Condensation Products of Furfuraldehyde with Succinic Acid. By FRITZ FICHTER and BEDA SCHEUERMANN (*Ber.*, 1901, **34**, 1626—1632).—In the presence of sodium ethoxide, furfuraldehyde and ethyl succinate condense to form furfurylidenesuccinic and difurfurylidenesuccinic acids, together with furfuryl alcohol and pyromucic acid. *Furfurylidenesuccinic acid*, $CO_2H\cdot C(CH\cdot C_4OH_3)\cdot CH_2\cdot CO_2H$, crystallises from water in long, yellowish needles decomposing at 205—215°. The *barium*, $C_9H_6O_5Ba,H_2O$, *calcium*, with H_2O, and *silver* salts all form needles. On reduction with sodium amalgam, furfurylcarbinylsuccinic acid is obtained (Abstr., 1900, i, 306). *Difurfurylidenesuccinic acid*, $C_{14}H_{10}O_6$, is much less soluble in water than the preceding acid, and crystallises in short prisms decomposing at 217—225°; the *barium* salt, with $3H_2O$, crystallises in compact prisms; the *calcium* salt, with $2H_2O$, in aggregates of needles, and the anhydrous *silver* salt in microscopic plates. On reduction with sodium amalgam, *difurfuryldicarbinylsuccinic acid*, $C_{14}H_{14}O_6$, is obtained as white crystals melting at 173°.

Furfuraldehyde condenses with sodium succinate in the presence of acetic anhydride to form *αβ-difurfurylidenepropionic acid*,

$$C_4OH_3{\cdot}CH{:}CH{\cdot}C({:}CH{\cdot}C_4OH_3){\cdot}CO_2H,$$

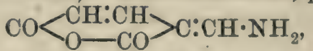
which forms yellow needles melting and decomposing at 195—197°, and is a very feeble acid. The *barium* salt, with $6H_2O$, forms flattened needles or plates; the *magnesium* salt, with $8H_2O$, small plates. On reduction, *α-furfurylcarbinyl-β-furfurylidenepropionic acid*,

$$C_4OH_3{\cdot}CH{:}CH{\cdot}CH(CH_2{\cdot}C_4OH_3){\cdot}CO_2H,$$

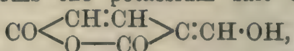
is obtained, and crystallises in small, white needles melting at 66—67°.

K. J. P. O.

isoCoumalic Acid. By Hans von Pechmann [with Max Hauser] (*Ber.*, 1901, **34**, 1406—1408).—iso*Coumalamide*, probably



$$CO{<}\genfrac{}{}{0pt}{}{CH{:}CH}{O{-}CO}{>}C{:}CH{\cdot}NH_2,$$

is obtained by the prolonged action of ammonia on methyl coumalate; it has a reddish tinge, melts and decomposes at 230—234°, and is insoluble in cold, aqueous sodium carbonate. When boiled with aqueous potassium carbonate, it forms the potassium salt of iso*coumalic acid*; this acid, probably  $CO{<}\genfrac{}{}{0pt}{}{CH{:}CH}{O{-}CO}{>}C{:}CH{\cdot}OH$, melts and decomposes at 170—180°, is a monobasic acid, gives a violet-red coloration with ferric chloride even in benzene solution, and reacts with methyl alcohol at the ordinary temperature to form a methyl ester.

C. F. B.

Action of Ethyl Iodide on Caffeine. By A. I. Rossolimo (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 247—249. Compare this vol., i, 161).—*Caffeine ethobromide*, $C_8H_{10}O_2N_4,EtBr$, prepared by the action of silver bromide on the ethiodide in alcoholic solution, separates from absolute alcohol as a colourless, drusy mass of short, four-sided prisms, and melts without becoming brown, but with evolution of gas bubbles, at 170—171°. It is stable in the dry state, but is slowly decomposed by water, from which it may be crystallised, although a diminished yield is thus obtained and the crystals obstinately retain traces of water. In regard to its stability towards the action of water, it occupies a position intermediate between the corresponding chloride and iodide.

T. H. P.

Conversion of the additive Compounds of Cinchonine with Hydrogen Haloids into Halogen-free Bases. By Zdenko H. Skraup (*Monatsh.*, 1901, **22**, 253—288. Compare Abstr., 1899, i, 961).—By the action of potassium hydroxide or silver nitrate on the additive compounds of cinchonine with hydrogen chloride, bromide, or iodide, a mixture of halogen-free bases is obtained, which are isomerides of cinchonine. Of this mixture of bases, a part is soluble in ether or 50 per cent. alcohol, and a part insoluble. The soluble portion consists chiefly of *α-iso*cinchonine, together with a small quantity of bases with one carbon atom less than cinchonine and its isomerides (compare this vol., i, 403); the insoluble portion consists mainly of *allo*cinchonine. The quantities of the *α-iso*cinchonine and difficultly soluble bases respectively have been determined; and the results are summarised in the following table. The quantities are expressed as percentages of the cinchonine used.

	Difficultly soluble. Bases.	*a-iso*Cinchonine.
Hydrochlorocinchonine decomposed by		
(1) Potassium hydroxide ……	13·3 per cent.	42·8 per cent.
(2) Silver nitrate ……………	31·9 ,,	33·0 ,,
Hydrobromocinchonine decomposed by		
(1) Potassium hydroxide ……	23·7 ,,	40·8 ,,
(2) Silver nitrate ……………	35·7 ,,	24·3 ,,
Hydroiodocinchonine decomposed by		
(1) Potassium hydroxide ……	40·8 ,,	22·3 ,,
(2) Silver nitrate ……………	59·8 ,,	15·6 ,,

In discussing these results, it is pointed out that the cause of the transformation of cinchonine and of the variation in the proportion of the two classes of bases cannot be found in the original additive products of the halogen acids with cinchonine. Each of these additive compounds is a single individual. The transformation of the cinchonine must occur during the withdrawal of the hydrogen haloid. Special experiments have shown, however, that neither potassium hydroxide nor silver nitrate can bring about any change in cinchonine or its isomerides; nor does variation of the concentration of the potash, &c., alter the relative proportion of the bases produced.

The author thinks that this group of bases (cinchonine, *a*- and *β-iso*cinchonine, and *allo*cinchonine) are not structural but stereo-isomerides, and discusses their relationship to each other (compare this vol., i, 404).
K. J. P. O.

Perbromides of Cinchona Alkaloids. By A. Christensen (*J. pr. Chem.*, 1901, [ii], **63**, 313—351).—The alkaloids quinine, cinchonine, and cinchonidine yield well crystallised bromine compounds, which are acid perbromides of alkaloid dibromides, $ABr_2.2HBr,Br_2$, and thus differ from the iodine derivatives AHI,I_2. One-sixth of the bromine is loosely combined and will set free iodine from potassium iodide, oxidise sulphurous acid, &c., and can thus be estimated.

Quinine dibromide hydrobromideperbromide, $C_{20}H_{24}O_2N_2Br_2,2HBr,Br_2$, prepared by adding excess of hydrobromic acid and then bromine to the solution of the alkaloid in acetic acid, crystallises in pale yellow, rhombic pyramids and prisms, which on heating decompose with the evolution of hydrogen bromide and a smell of quinoline. This substance is readily soluble in alcohol and can be crystallised from acetic acid. To aqueous sodium carbonate, 4 atoms of bromine are given up, whilst alcoholic potash withdraws the whole of the halogen. A *mercury* double salt, $C_{20}H_{24}O_2N_2Br_2.2HBr,HgBr_2$, obtained by rubbing the perbromide with mercury, crystallises in prismatic needles.

Quinine dibromide (Comstock and Koenigs, Abstr., 1892, 1010), is obtained from the perbromide by removing bromine with sulphurous acid, and then precipitating the base with sodium hydroxide. The

nitrate, $C_{20}H_{14}O_2N_2Br_2,2HNO_3$, forms rhombic prisms very insoluble in water (*loc. cit.*). *Dibromoherapathite*, $4C_{20}H_{14}O_2N_2Br_2,3H_2SO_4,2HI,I_4$, crystallises in thin plates very closely resembling herapathite.

Cinchonidine dibromide hydrobromide perbromide,

$$C_{19}H_{22}ON_2Br_2,2HBr,Br_2,$$

crystallises in pale yellow, quadratic plates. With mercury it yields the double salt, $C_{19}H_{22}ON_2Br_2,2HBr,HgBr_2$, crystallising in needles. *Cinchonidine dibromide*, $C_{19}H_{22}ON_2Br_2$, crystallises in six-sided plates or rhombic leaflets, and begins to decompose at 180°. It does not give the quinine reaction with bromine and ammonia. The *hydrochloride*, $C_{19}H_{22}ON_2Br_2,2HCl,2H_2O$, forms prismatic needles; the *hydrobromide*, $C_{19}H_{22}ON_2Br_2,2HBr,2H_2O$, prismatic needles; the *sulphate*,

$$C_{19}H_{22}ON_2Br_2,H_2SO_4,6H_2O\ (?),$$

slender needles; the *nitrate*, $C_{19}H_{22}ON_2Br_2,2HNO_3,H_2O$, rhombic plates.

Cinchonine dibromide hydrobromide perbromide,

$$C_{19}H_{22}ON_2Br_2,2HBr,Br_2,$$

is obtained as small, yellow, prismatic needles, which give off bromine on standing in the air, leaving the hydrobromide. The *mercury* double salt, $C_{19}H_{22}ON_2Br_2,2HBr,HgBr_2$, forms long, white, prismatic needles.

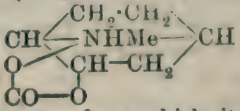
Cinchonine dibromine, obtained from the perbromide, is identical with the base prepared by Comstock and Koenigs (*loc. cit.*); the *hydrobromide*, $C_{19}H_{22}ON_2Br_2,2HBr$, crystallises in rhombic plates.

The salts of these alkaloids, when treated with a solution of potassium iodide and potassium iodate, set free a quantity of iodine equivalent to half the acid present in the salt. One mol. of the acid is therefore more loosely combined than the other. These salts are consequently acid salts, and the alkaloids are mono-acid. K. J. P. O.

Basic Quinine "Saccharinate." By H. Défournel (*Bull. Soc. Chim.*, 1901, [iii], 25, 606—607).—*Basic quinine "saccharinate,"* obtained by double decomposition from quinine sulphate and the sodium derivative of "saccharin" (*o*-benzoicsulphinide), crystallises from methyl alcohol in needles of the composition

$$C_7H_5O_3NS,C_{20}H_{24}O_2N_2,H_2O,$$

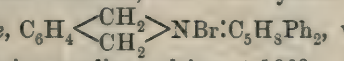
which melt and decompose at 194—195°. It is almost insoluble in cold water, but more soluble in boiling water (1 part in 130) and in organic solvents. N. L.

Conversion of Tropinone into *r*-Cocaine. By Richard Willstätter and Adolf Bode (*Ber.*, 1901, 34, 1457—1461).—The chief product of the action of sodium amalgam on sodium tropinonecarboxylate is *ψ-tropinecarbonic acid*, which probably has the betaine structure, ; it is insoluble in ether, but readily soluble in water, from which it crystallises in glistening, hexagonal, monosymmetric tablets containing $3H_2O$; when dried over sulphuric acid it melts and decomposes at 201—202°; it has a neutral reaction, is stable towards potassium permanganate, and has a normal molecular weight in aqueous solution. The *hydrochloride*, $C_9H_{15}O_3N,HCl$, crystallises from alcohol in monoclinic tablets, and melts and decomposes at 239°; the *aurichloride* crystallises in needles, and melts and decomposes at 174—176°. The acid does not give an ester, but is converted by hydrogen chloride in alcoholic or aqueous solution into ψ-tropine.

An *inactive ecgonine*, probably racemic ecgonine, is produced as a bye-product in the reduction of tropinecarboxylic acid; it separates from alcohol in anhydrous, rhombic crystals, has a neutral reaction, is stable towards permanganate, and melts and decomposes at 251°. The *hydrochloride* forms slender, white needles containing $\frac{1}{2}H_2O$, becomes anhydrous at 120°, melts with frothing at 149°, and is more soluble in alcohol than the hydrochloride of the carbonic acid; the *aurichloride* forms glistening needles, is more soluble than the isomeride, and melts and decomposes at 213°. The *methyl* ester crystallises from ethyl acetate in needles, and melts at 125°; the *methiodide* of the ester is readily soluble in water, crystallises in needles, melts at 182°, and is converted by warm alkalis into *cyclo*heptatrienecarboxylic acid. r-*Cocaine* crystallises from light petroleum in hexagonal plates, and melts at 80°; it forms a picrate, aurichloride, and platinichloride, and like *d*-cocaine, but unlike *l*-cocaine, gives a sparingly soluble nitrate. The *hydrochloride* crystallises from alcohol in transparent tablets and melts and decomposes at 194°. Synthetical cocaine has the same physiological action as the natural product.

T. M. L.

Stereoisomeric 2 : 6-Diphenylpiperidines. By Max Scholtz (*Ber.*, 1901, **34**, 1616—1623. Compare Abstr., 1895, i, 563; Paal, *ibid.*, 1896, i, 389).

—The base obtained by the reduction of 2 : 6-diphenylpyridine is a mixture of two stereoisomeric diphenylpiperidines, the one oily, and the other melting at 71°. The two are most readily separated by the fractional crystallisation of their hydrochlorides, as the salt of the oily base, which melts at 218°, is much more soluble than that of the solid, which melts at 316°. 2 : 6-Diphenylpiperidine melts at 71°, and distils at 206—207° under 15 mm. pressure. The *hydrobromide* crystallises in long needles melting at 295°, the *hydriodide* melts at 248°, and is only sparingly soluble in water at 25°. The acid *sulphate*, $C_{17}H_{19}N,H_2SO_4$, crystallises in plates, and melts at 255°, the picrate melts at 212°, not 198° as previously stated, and the *benzoyl* derivative crystallises in prisms melting at 137°. When treated with *o*-xylylene bromide, the base yields *xylylenediphenylpiperidonium bromide*,  $C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>NBr{:}C_5H_8Ph_2$, which crystallise from alcohol in glistening needles melting at 190°.

The oily base, *iso*-2 : 6-diphenylpiperidine, does not solidify when placed in a freezing mixture, distils at 204—205° under 15 mm. pressure, and has a sp. gr. 1·0657 at 20°/4°. The *hydrochloride* crystallises in colourless needles, and melts at 218°, the *hydrobromide* melts at 258°, the *hydriodide* at 257°, the *acid sulphate*, which is readily soluble in water, at 192°, the *benzoyl* derivative at 115°, and the *xylylenediphenylpiperidonium bromide* at 135°. The picrate is an oil. All attempts to resolve either of the two bases into optically active constituents have so far failed. J. J. S.

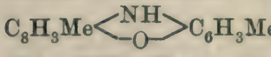
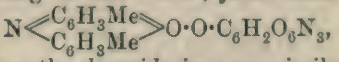
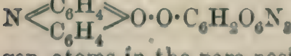
Action of Benzyl Chloride and Iodide on Pyridine. By A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 249—258).—*Pyridine benzyl iodide*, C_5H_5N,CH_2PhI,H_2O, separates from 95 per cent. alcohol, by cooling or adding ether, in pale yellow crystals which melt at 97° and are soluble in water or alcohol.

By the action of excess of pyridine on benzyl chloride or iodide, a mixture of 2-and 3-benzylpyridines is obtained, the former predominating if the chloride is used, and the latter if the iodide.

2-*Benzylpyridine*, $C_{12}H_{11}N$, boils at 276° under 742 mm. pressure, and on cooling becomes viscid, but does not crystallise; it has a not unpleasant odour, somewhat resembling that of lemons and mixes with alcohol or ether; it has the sp. gr. 1·0536 at 20°/0° and 1·0756 at 0°/0°. When oxidised with acid permanganate, it yields picolinic acid. Its salts with mineral acids are mostly readily soluble in water and difficult to crystallise; its *platinichloride* separates from water in large, orange crystals melting at 183°, and its *picrate* is deposited from alcohol in sparkling, strongly refractive, yellow crystals melting at 140°.

3-*Benzylpyridine*, boiling at 287° under 742 mm. pressure, resembles the 2 compound, but has a stronger and unpleasant smell; it has the sp. gr. 1·0614 at 20°/0° and 1·0756 at 0°/0°. Oxidation with acid permanganate gives *iso*nicotinic acid. It forms readily soluble salts with mineral acids; its *platinichloride* separates from water in golden-yellow leaflets melting at 207°, and the *picrate* crystallises from benzene in large, shining, plastic needles melting at about 136—138°.

Besides the two benzylpyridines, the action of benzyl chloride or iodide on pyridine yields a small quantity of higher boiling bases, probably dibenzylpyridines, together with neutral products which are being investigated. T. H. P.

Azoxonium Compounds. By FRIEDRICH KEHRMANN (*Ber.*, 1901, **34**, 1623—1626).—Methylcatechol [$Me:(OH)_2 = 1:3:4$] and *o*-amino-*m*-cresol react at 250—260°, yielding two isomeric *dimethylphenoxazines*,  $C_8H_3Me<{NH \atop O}>C_6H_3Me$, the one melting at 179° and the other at 204—205°. The reaction proceeds more readily than in the preparation of phenoxazine itself (Bernthsen, Abstr., 1887, 665). When oxidised with ferric chloride or bromine, the two compounds, especially the one melting at 204—205°, yield salts of *dimethylphenoxazonium*. The *picrate*,  $N<{C_6H_3Me \atop C_6H_3Me}>O\cdot O\cdot C_6H_2O_6N_3$, forms a reddish-violet crystalline powder, the *bromide* is very similar. *Phenoxazonium picrate*,  $N<{C_6H_4 \atop C_6H_4}>O\cdot O\cdot C_6H_2O_6N_3$, is an unstable, brick-red powder; its hydrogen atoms in the para-positions to the tervalent nitrogen are readily replaceable by amino- or substituted amino-groups, yielding different coloured dyes. Phenanthroxazine (this vol., i, 280), when oxidised with bromine in nitrobenzene solution, yields *phenanthrazoxonium per-*

bromide, $C_{28}H_{16}ONBr_3$, in the form of dark blue plates with a coppery lustre.
J. J. S.

[Method of] Avoiding the Formation of Bases containing Chlorine in the Reduction of Aromatic Nitro-compounds with Tin and Hydrochloric Acid. By Johannes Pinnow (*J. pr. Chem.*, 1901, [ii], 63, 352—363).—When the reduction is carried out by tin and hydrochloric acid in the presence of a piece of graphite, it is found possible to operate in dilute solution and thus avoid that rise of temperature which is favorable to the production of chloro-bases. Thus 3-nitrodimethyl-*p*-toluidine under these conditions yields more dimethyltolylenediamine, and less chlorodimethyltolylenediamine, than when reduced by the ordinary method. Further, no 1 : 5-dimethylbenziminazole is formed at a temperature of 17° by this method, and only 3·3 per cent. at a temperature of 50—55°.

The *double* salt of 3-nitrodimethyl-*p*-toluidine hydrochloride and stannic chloride, $4C_9H_{12}O_2N_2,4HCl,SnCl_4,3H_2O$, is very insoluble in water and melts and decomposes at 230—231°.

1 : 5-*Dimethylbenziminazole tartrate*, $C_8H_{10}N_2,C_4H_6O_6,4H_2O$, forms needles melting at 187·3—188°.

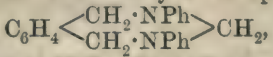
When the reduction is carried out by Löb's method (Abstr., 1896, i, 533), using graphite instead of platinum, chloro-bases are always formed and 30 per cent. of dimethylbenziminazole is produced.

The reduction of nitromethylaziminotoluene was also investigated. To obtain this substance, 3 : 5-dinitromethyl-*p*-toluidine was obtained by the action of 55 per cent. nitric acid containing nitrous acid on dimethyl-*p*-toluidine. On reduction of the dinitro-compound with ammonium sulphide, 3-*nitromethyltolylene*-4 : 5-*diamine*,

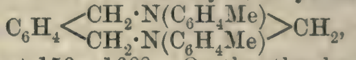
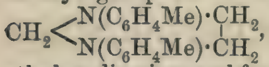
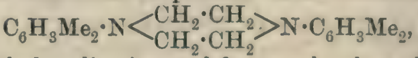
$$NO_2{\cdot}C_6H_3Me(NH_2){\cdot}NHMe,$$

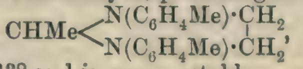
is produced and crystallises in bluish-red plates, or short prisms melting at 131·5—132·5°. 7-*Nitro*-1-*methylaziminotoluene*, prepared from the diamine by the action of nitrous acid, forms light brown needles melting at 174·5—175·5°. Reduction in the ordinary way with tin and hydrochloric acid produced 1-*methylaziminochlorotoluidine*, $C_8H_9N_4Cl$, melting at 189—190°. Reduction with zinc dust and acetic acid, followed by the addition of benzaldehyde to the reduced product, yields *benzylidene*-1-*methylazimino*-m-*toluidine*, forming yellowish-green needles melting at 151·5—152·5°. On boiling this substance with concentrated hydrochloric acid, a sparingly soluble base, melting at 278°, and *amino*-1-*methylaziminotoluene*, $NH_2{\cdot}C_6H_3Me{\cdot}N_3Me$, are formed. The latter crystallises in white needles melting at 133·5°, and forms a *hydrochloride*, $C_8H_{10}N_4,HCl,H_2O$.

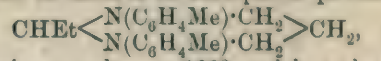
On reducing 7-nitro-1-methylaziminotoluene with tin and hydrochloric acid in the presence of graphite, at a temperature finally of 46°, a mixture of chloro-base and amino-1-methylaziminotoluene is obtained which cannot be separated. With benzenediazonium chloride, the mixture yields the hydrochloride of *benzeneazoaminomethylaziminotoluene*, $C_{14}H_{14}N_6$, which forms orange needles melting at 202°.
K. J. P. O.

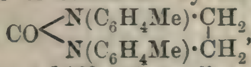
Action of Aldehydes and of Carbonyl Chloride on Diamines. By Max Scholtz and K. Jaross (*Ber.*, 1901, 34, 1504—1513).—The object of the following experiments was to ascertain the influence of substituents in various positions in aromatic diamines on the reaction between these and the aldehydes. Diphenyl *o*-xylylenediamine readily reacts with formaldehyde to produce *diphenyl-*o*-xylylenemethylenediamine*,  $C_6H_4<\begin{array}{l}CH_2{\cdot}NPh\\CH_2{\cdot}NPh\end{array}>CH_2$, which crystallises in colourless needles melting at 196°. *Di-*p*-tolyl-*o*-xylylenediamine*,

$$C_6H_4(CH_2{\cdot}NH{\cdot}C_6H_4Me)_2,$$

is formed together with *p*-tolyldihydro*iso*indole, when *o*-xylylene bromide is treated with an excess of *p*-toluidine, and crystallises in colourless plates melting at 112°. With formaldehyde, it yields *di-*p*-tolyl-*o*-xylylenemethylenediamine*,  $C_6H_4<\begin{array}{l}CH_2{\cdot}N(C_6H_4Me)\\CH_2{\cdot}N(C_6H_4Me)\end{array}>CH_2$, which crystallises in plates melting at 159—160°. On the other hand, di-*o*-tolyl-*o*-xylylenediamine does not form a condensation product with formaldehyde, and this is probably due to the stereochemical effect of the methyl group in the *o*-position. 1 : 3-*Di-*p*-tolyltetrahydroglyoxaline*,  $CH_2<\begin{array}{l}N(C_6H_4Me){\cdot}CH_2\\ \qquad\qquad\quad\,|\\N(C_6H_4Me){\cdot}CH_2\end{array}$, is obtained from formaldehyde and di-*p*-tolylethylenediamine, and forms colourless tablets melting at 176°. 1 : 3-*Di-*m*-tolyltetrahydroglyoxaline* is prepared in a similar manner from di-*m*-tolylethylenediamine, and crystallises in colourless prisms melting at 100—101°. Di-*o*-tolylethylenediamine also appears to react with formaldehyde, but no crystalline product could be isolated from the mass produced. *Dixylylethylenediamine*, $C_2H_4(NH{\cdot}C_6H_3Me_2)_2$, is obtained by heating *as*-*m*-xylidine with ethylene bromide and sodium carbonate, and crystallises in colourless needles melting at 71°. It yields no crystalline condensation product with formaldehyde. 1 : 4-*Dixylylpiperazine*,  $C_6H_3Me_2{\cdot}N<\begin{array}{l}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{array}>N{\cdot}C_6H_3Me_2$, is formed along with dixylylethylenediamine, and forms colourless plates melting at 150°.

m-Tolylethylenediamine reacts with acetaldehyde in a similar manner to formaldehyde, producing 1 : 3-*di-*m*-tolyl-2-methyltetrahydroglyoxaline*,  $CHMe<\begin{array}{l}N(C_6H_4Me){\cdot}CH_2\\ \qquad\qquad\quad\,|\\N(C_6H_4Me){\cdot}CH_2\end{array}$, which forms colourless needles melting at 83° and is very unstable.

Di-*p*-tolyltrimethylenediamine does not react with formaldehyde, whilst diphenyltrimethylenediamine undergoes the normal reaction. These two bases, however, do not differ in their behaviour towards other aldehydes. Di-*p*-tolyltrimethylenediamine readily reacts with propaldehyde, forming two compounds of the same percentage composition. One of these is an amorphous powder melting at 98°, whilst the second,  $CHEt<\begin{array}{l}N(C_6H_4Me){\cdot}CH_2\\N(C_6H_4Me){\cdot}CH_2\end{array}>CH_2$, crystallises in short, colourless prisms, melts at 268°, and has the molecular weight corresponding with the formula given, according to which it is 1 : 3-*tolyl-2-ethylhexahydropyrimidine*. Diphenyltrimethylenediamine also yields two compounds with propaldehyde, one of which melts at about 90°, and the other at 250°. These have not yet been more closely examined.

Di-*m*-tolylethylenediamine is converted by carbonyl chloride into *di*-m-*tolylethylenecarbamide*,  $CO<\begin{matrix}N(C_6H_4Me)\cdot CH_2\\ \quad\quad\quad\quad\quad\ \vert\\ N(C_6H_4Me)\cdot CH_2\end{matrix}$, which forms colourless, lustrous plates melting at 146°. A small amount of a *dichloride* is also produced. Di-*o*-tolylethylenediamine, on the other hand, does not yield a cyclic carbamide derivative, but only the *dichloride* of *di-o-tolylethylenedicarbamic acid*, $C_2H_4[N(COCl)\cdot C_6H_4Me]_2$, which crystallises in colourless needles melting at 163°. Sodium ethoxide converts it into *di-o-tolylethylenediurethane*, $C_2H_4[N(CO_2Et)\cdot C_7H_7]_2$, which is a colourless, crystalline powder melting at 79°. This difference between the behaviour of the *m*-compound and the corresponding *o*-derivative is also to be referred to the stereochemical effect of the *o*-methyl group. A. H.

Electrolytic Preparation of Benzidine. By WALTHER LÖB (*Zeit. Elektrochem.*, 1901, 7, 597—603. Compare Abstr., 1900, i, 697).—Under certain conditions, azoxybenzene may be reduced to benzidine with a yield of 64 to 70 per cent. Azoxybenzene (2 grams) is suspended in 25·75 per cent. hydrochloric acid (70 c.c.) containing stannous chloride (1—1·5 grams) in solution, the liquid is placed in a porous pot standing in hydrochloric acid; the cathode is formed of pure nickel gauze, and it is also used as a stirrer in order to keep the azoxybenzene in suspension. The cathodic current density may vary from 0·008 to 0·05 ampere per sq. cm., and the temperature from 60° to 90°. Little or no benzidine was obtained when other salts were added to the solution, or other metals used as cathodes. T. E.

Action of "Saccharin" on Phenylhydrazine Ureide [Phenylcarbazide]. By H. DÉFOURNEL (*Bull. Soc. Chim.*, 1901, [iii], **25**, 604—606).—Phenylcarbazide reacts with "saccharin" (*o*-benzoicsulphinide) in methyl alcohol solution to form a *compound*,

$$NHPh\cdot NH\cdot CO\cdot NH\cdot NPh\cdot CO\cdot C_6H_4\cdot SO_2\cdot NH_2,$$

which crystallises in slender, white needles melting at 98°, and is decomposed by dilute sulphuric acid, or by prolonged boiling with water, with the formation of *o*-sulphaminobenzoic acid. N. L.

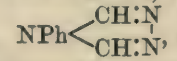
Thiourea-amidines. By HENRY L. WHEELER (*J. Amer. Chem. Soc.*, 1901, **23**, 223—227).—Wheeler and Sanders (Abstr., 1900, i, 563) have shown that, by the action of organic bases on ureaimino-esters, amidines are produced; this is now confirmed by the preparation of phenylbenzenylureaphenylamidine from phenylcarbimide and phenylbenzenylamidine, the product being identical with that previously described.

On the other hand, the compounds obtained (*loc. cit.*) by the action of phenyl- and benzoyl-thiocarbimides on imino-esters, and supposed to be phenylbenzenylthiourea-*p*-anisylamidine, the corresponding phenyl and *β*-naphthyl derivatives, benzoylbenzenylthioureaphenylamidine and the analogous *o*-tolyl derivative, are found, on further investigation, to be phenyl-*p*-anisyl-, diphenyl-, phenyl-*β*-naphthyl-, phenylbenzoyl-, and *o*-tolylbenzoyl-thiocarbamides respectively.

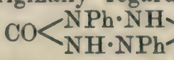
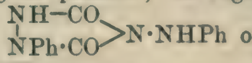
The true *phenylbenzenylthioureaphenylamidine*,

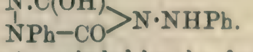
$$NHPh\cdot CPh{:}N\cdot CS\cdot NHPh,$$

obtained by the action of phenylthiocarbimide on phenylbenzenylamidine, crystallises from benzene in slender needles or prisms and melts at 138°; it is quite different to the product previously described under this name. Benzoylthiocarbimide reacts with phenylbenzenylamidine to form a crystalline substance melting at 162°. E. G.

Synthesis of 1:3:4-Triazole Derivatives. By Guido Pellizzari and C. Massa (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 363—367).—1-*Phenyl*-1 : 3 : 4-*triazole*,  $NPh<\begin{array}{l}CH:N\\ CH:N\end{array}$, may be obtained by the interaction of (1) formylhydrazide and formanilide, (2) diformylhydrazide and formanilide, (3) diformylhydrazide and aniline, or (4) aniline (1 mol.), hydrazine (1 mol.), and formic acid (2 mols.); it separates from benzene in long needles, or from water in hard prisms, melting at 121°, distils with partial decomposition, and dissolves readily in water or alcohol. It has no action on litmus paper, but has basic properties, and forms well-defined salts; with copper sulphate it gives a pale azure precipitate, and with mercuric chloride or silver nitrate a white precipitate. Its *platinichloride* separates in yellow needles, and on boiling in dilute aqueous solution yields the compound $(C_8H_7N_3)_2PtCl_4$ as an amorphous, yellow, insoluble powder; the *picrate* separates from alcohol in slender, yellow needles melting at 169°.

[With Paoletti.]—Introduced in any way into the animal (frogs and dogs) system, it acts as an excitant, producing palpitation, muscular shock, convulsions, and convulsive fits, varying in duration and intensity according to the dose administered. The minimum lethal dose is 0·06 gram per kilogram weight of animal. It thus closely resembles strychnine in its action and toxic power. T. H. P.

Constitution of the Urazines. By Max Busch (*Chem. Centr.*, 1901, i, 933—937; from *Festschrift*, Erlangen, 1901).—Diphenylurazine was originally regarded as symmetrical diphenyldiketohexahydrotetrazine,  $CO<\begin{array}{l}NPh\cdot NH\\ NH\cdot NPh\end{array}>CO$ (Pinner, Abstr., 1888, 1084; Heller, Abstr., 1891, 1213), of which the parent substance is diphenylcarbamide (Curtius and Heidenreich, Abstr., 1895, i, 12). Later, the formula $CO<\begin{array}{l}NH\cdot NPh\\ NH\cdot NPh\end{array}>CO$, or the tautomeric monohydroxy-modification of this, was assigned to it (Rupe, Abstr., 1896, i, 429; 1899, i, 356). From experiments described below, the author concludes that a triazole and not a tetrazine ring is present; he regards diphenylurazine as phenylanilinourazole,  $\begin{array}{l}NH-CO\\ NPh\cdot CO\end{array}>N\cdot NHPh$ or


$$\begin{array}{l}N:C(OH)\\ NPh-CO\end{array}>N\cdot NHPh.$$

A symmetrical constitution is excluded by the fact that isomeric products are obtained when, in one case a phenyl compound is taken and tolyl introduced, and in the other phenyl is introduced into a tolyl compound. The absence of basic properties is remarkable in diphenylurazine and its alkyloxy-derivatives; but then substances are obtained, by analogous methods, from unsymmetrical dialkylhydrazines, and these have no basic properties either, although they must contain a five atom ring. Again, ethyl diphenylcarbazidedicarboxylate, $CO(NPh\cdot NH\cdot CO_2Et)_2$, which could hardly form the five-membered ring, does not in fact condense to diphenylurazine. Further, the formation of a benzylidene derivative of monophenylurazine is difficult to understand if the presence of a six-membered ring is assumed; and the reaction of monoarylurazines with nitrous acid is analogous to that of unsymmetrical disubstituted hydrazines in general.

Ethyl 2 : 5-*diphenylcarbazide*-1-*carboxylate*,

$$NHPh\cdot NH\cdot CO\cdot NPh\cdot NH\cdot CO_2Et,$$

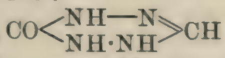
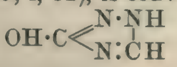
from ethyl chlorocarbonylphenylcarbazinate, $COCl\cdot NPh\cdot NH\cdot CO_2Et$ (Abstr., 1899, i, 957), and phenylhydrazine, melts at 186° and has no basic properties; it forms a yellowish, unstable, *mononitroso*-derivative decomposing at 121—122°. When heated at 200°, or digested with very dilute aqueous sodium hydroxide at 40—50°, it is converted quantitatively into phenylanilinourazole (diphenylurazine), which can also be prepared by warming diphenylcarbazide, $CO(NH\cdot NHPh)_2$, and ethyl chloroformate with pyridine in benzene solution. This substance is a strong acid, dissolving even in aqueous alkali carbonates and ammonia; from these solutions, it is precipitated by mineral acids, but not by acetic acid. It forms *methyl* and *benzyl ethers* melting at 153° and 176—177° respectively; these have no acid character. It and the methyl ether form *nitroso*-derivatives which melt at 120° and 89—90°; the *nitrosoamine* formed from the benzyl ether is oily.

By analogous methods, the following compounds were prepared; the numbers given are their melting points. *Ethyl* 2-*phenyl*-5-p-*tolylcarbazide*-1-*carboxylate*, 200°; *phenyl*-p-*toluinourazole*, 238°, its *acetyl* derivative, 146—147°. The isomeric 5-*phenyl*-2-p-*tolyl* compounds, 174—175°, 239·5°, and 170° respectively. *Ethylchlorocarbonyl*-p-*tolylcarbazinate*, 94°. *Phenylanisidinourazole*, 205·5°; the isomeric *anisylanilinourazole*, 242°.

Urazoles were also obtained from ethyl chlorocarbonylphenylcarbazinate by the action of methylhydrazine and of *as*-diethyl- and dibenzyl-hydrazines. Phenylmethylaminourazole has been described already as phenylurazine (Abstr., 1900, i, 314); its methyl ether forms a *benzylidene* compound melting at 139—140°.

Ethyl 2-*phenyl*-5-*diethylcarbazide*-1-*carboxylate*, 195—196°; some ethoxyphenyldiazolone (Abstr., 1899, i, 957) is formed along with it. *Phenyldiethylaminourazole*, 137—138°; its *ethyl ether*, 76°.

Ethyl 2-*phenyl*-5 *dibenzylcarbazide*-1-*carboxylate*, 135—136°. *Phenyldibenzylaminourazole*, 185—186°.

Methenylcarbohydrazide,  $\mathrm{CO}<\begin{smallmatrix}\mathrm{NH—N}\\ \mathrm{NH\cdot NH}\end{smallmatrix}>\mathrm{CH}$ (Curtius and Heidenreich, Abstr., 1895, i, 12), is converted by nitrous acid into 3-hydroxy-1 : 2 : 4-triazole,  $\mathrm{OH\cdot C}<\begin{smallmatrix}\mathrm{N\cdot NH}\\ \mathrm{N:CH}\end{smallmatrix}$ (Widman and Cleve, Abstr., 1898, i, 335).

C. F. B.

Dyes for Fats. By Leonor Michaelis (*Virchow Arch.*, 1901, **164**, 263—270).—By a series of comparative experiments, the author has found that only azo-compounds which possess no salt-forming group are capable of dyeing fats. Thus soudan III (azobenzene-azo-β-naphthol), benzene-azo-β-naphthol, benzene-azo-*p*-cresol, azo-*o*-tolueneazo-β-naphthol, and benzeneazophenetole, which are all insoluble in alkalis, all dye fats, whereas benzeneazo-α-naphthol and benzene-azo-*o*-cresol, which are soluble in alkalis, do not act in this way. A number of these chemically indifferent dyes just mentioned are derivatives of phenols, but as they are insoluble in alkalis they probably have the tautomeric quinone structure. The benzidine dyes, such as diphenyltetrazodi-β-naphthol and diphenyltetrazodi-*p*-cresol, which are also insoluble in alkalis, also act as dyes, but are not practically convenient. The most suitable of all is azo-*o*-toluene-azo-β-naphthol, $C_6H_4Me{\cdot}N_2{\cdot}C_6H_3Me{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$, which is sold as scarlet R, or "Fett ponceau." A. H.

Proteids. By IVAR BANG (*Zeit. physiol. Chem.*, 1901, **32**, 79—80). By ALBRECHT KOSSEL (*ibid.*, 81).—Polemical. J. J. S.

Proteids. By ADOLF JOLLES (*Ber.*, 1901, **34**, 1447—1448; *Zeit. physiol. Chem.*, 1901, **32**, 361—392).—Four types of nitrogen compounds are produced by the oxidation of proteids (this vol., i, 262), namely, (1) ammonia (traces only), (2) carbamide, (3) substances such as methylamine and aminoacetic acid which are precipitated by phosphotungstic acid, (4) substances not precipitated by phosphotungstic acid. The proportions of nitrogen in each form found were as follows:

	(2)	(3)	(4)	Total.
Crystallised egg-albumin ...	11·80	3·12	—	14·98
Crystallised serum-globulin .	12·00	3·93	—	15·94
Crystallised serum-albumin .	12·97	3·18	—	16·04
Oxyhæmoglobin	15·43	1·50	—	16·91
Casein	11·12	3·90	—	15·30
Fibrin	7·56	4·09	4·87	16·64
Vitellin from yolk of egg ...	11·96	3·21	—	15·30
Vitellin from plants	8·22	3·23	6·19	17·98

The production of carbamide in quantities varying from 45 to 90 per cent. of the total nitrogen is of importance as indicating the presence of –CO·NH– groups. T. M. L.

Breaking down of Albuminoids or Protoplasmides. By ALEXANDRE ÉTARD (*Compt. rend.*, 1901, **132**, 1184—1187).—When decalcified beef bone is boiled with dilute sulphuric acid (20 : 100) for several hours and the product is treated with excess of barium hydroxide, it yields glycine, leucine, a little tyrosine, a syrupy substance very soluble in methyl alcohol, and a deliquescent substance, which is quite insoluble in methyl alcohol and has the composition

$$C_{18}H_{41}O_{20}N_5Ba_2.$$

When the barium is removed from the latter by treatment with sulphuric acid and methyl alcohol, a white, deliquescent, granular, crystalline substance of the composition $C_{18}H_{35}O_{15}N_5$ is obtained, which the author calls *bos-osteoplasmide*. One mol. combines with one mol. of barium oxide, yielding $C_{18}H_{35}O_{15}N_5,BaO$. The author regards these substances, derived from albuminoids or protoplasmides, as nitrogenous saccharides, the hydrolysis of the albuminoids being analogous to that of the condensed saccharides. C. H. B.

Detection of Cystin and of Cystein in the decomposition Products of Proteids. By GUSTAV EMBDEN (*Zeit. physiol. Chem.*, 1901, **32**, 94—103. Compare Mörner, *ibid.*, **28**, 595).—The author adopts a somewhat modified form of Mörner's latest method for the isolation of cystin. Horn shavings are boiled for several hours with concentrated hydrochloric acid, neutralised with sodium hydroxide, kept for 24 hours, filtered, the filtrate slightly acidified with hydrochloric acid, and evaporated to crystallisation. The crystals are first treated with water, and then with very dilute nitric acid in order to remove admixed tyrosine. Cystin may also be isolated in the form of its insoluble *copper* salt, which crystallises in at least two distinct forms. Cystein is also present in the products formed when serum-albumin, egg-albumin, or edestin is boiled with hydrochloric acid. J. J. S.

Combination of Fat and Proteid. By JOSEPH NERKING (*Pflüger's Archiv*, 1901, **85**, 330—344).—After removal of the fat from proteid by a Soxhlet's apparatus, and subsequent peptic digestion, the residue yielded no ethereal extract in the majority of proteid materials investigated, namely, serum-albumin, proteids of muscle, casein, lactalbumin, oxyhæmoglobin, egg-albumin, ovomucoid, and various vegetable proteids. A few proteid substances like mucin and serum-globulin gave a small yield of ethereal extract (fat) in the same circumstances. Whether this fat is in chemical union with the proteid is not proved. W. D. H.

Formation of Urea by the Oxidation of Albumin by means of Ammonium Persulphate. By LOUIS HUGOUNENQ (*Compt. rend.*, 1901, **132**, 1240—1241).—To ammoniacal aqueous solutions of egg-albumin maintained at a temperature of 90°, sufficient ammonium persulphate is added to completely oxidise the albumin. From the product of the reaction, urea was isolated, by evaporating, and extracting with alcohol-ether; it represents 5 per cent of the albumin oxidised.

K. J. P. O.

Optical Activity of Lecithin. By C. ULPIANI (*Atti Real. Accad. Lincei*, 1901, [v], **10**, i, 368—375).—For the preparation of lecithin from yolk of egg, the author makes use of Strecker's method of extraction with a mixture of alcohol and ether. The distillation of the latter is, however, done away with, as in the event of the lecithin being optically active the heating would be liable to cause racemisation. The lecithin is separated in the form of its cadmiochloride, which, after purification, is suspended in alcohol and treated with either lead hydroxide or moist silver oxide; in the latter case, a solution perfectly free from cadmium or chlorine is obtained. This solution of lecithin is dextrorotatory, but it was not found possible to separate from it an appreciable quantity of lecithin, although voluminous white flocks are precipitated when the liquid is cooled by means of solid carbon dioxide and liquid air. For the rotation of the cadmiochloride, determined in alcoholic carbon disulphide, the following numbers were obtained: $[a]_D^{24°}$ (c 0·9968) + 11·41°; $[a]_D^{26°}$ (c 1·9936) + 11·41°; $[a]_D^{24°}$ (c 3·0224) + 11·29°.

These results show that lecithin is really optically active, the inactive products previously obtained being due to racemisation brought about by heating during the preparation. The asymmetric formula must hence be assigned to lecithin, which is the first mixed compound ether known to exhibit optical activity. T. H. P.

Spectral Reactions of Blood in presence of Formaldehyde. By BERNHARD TOLLENS (*Ber.*, 1901, **34**, 1426—1427).—The difficulty of observing the absorption band of the reduced hæmoglobin of blood, which is broader but weaker than those of oxyhæmoglobin, is removed if formaldehyde is added to the liquid. The presence of this compound does not interfere in the slightest degree with the two oxyhæmoglobin absorption bands, but when the solution is gently heated with ammonium sulphide, these two bands gradually disappear and almost exactly midway between them a third black band of nearly the same intensity comes into view. If now the cooled liquid is shaken in the air, this new band vanishes and the two oxyhæmoglobin bands reappear; the latter give way to the middle band when the liquid is warmed, and so on. In presence of carbon monoxide, this action of formaldehyde does not take place, for the two carbon monoxide-hæmoglobin bands then persist even after warming with ammonium sulphide.

T. H. P.

Hexon Bases in Heteroalbumose and in Peptone (Deuteroalbumose). By H. C. HASLAM (*Zeit. physiol. Chem.*, 1901, **32**, 54—58).—Kossel and Kutscher's method for estimating hexon bases has been employed in the case of heteroalbumose and also of deuteroalbumose, both of which were obtained from Witte's peptone.

The percentages found were:

	Histidine.	Arginine.	Lysine.	Ammonia.	Humin nitrogen.
Deuteroalbumose ...	1·5	7·1	6·9	0·98	6·5
Heteroalbumose	2·2	4·9	3·5	0·79	14·8

J. J. S.

Preparation of pure Amphopeptone. By PAUL MÜHLE (*Chem. Centr.*, 1901, i, 1205; from *Diss. Leipzig*).—By employing Siegfried's method of precipitating the iron salts (this vol., i, 57) two peptones, $C_{21}H_{34}O_9N_6$ and $C_{21}H_{36}O_{10}N_6$, have been isolated from the product of the peptic digestion of fibrin. The pure amphopeptones form white powders, are not deliquescent, and have distinctly acid characters. They do not form silver salts of constant composition, but the barium salts, $(C_{21}H_{33}O_9N_6)_2Ba$ and $(C_{21}H_{35}O_{10}N_6)_2Ba$, and the zinc salts, $(C_{21}H_{33}O_9N_6)_2Zn$ and $(C_{21}H_{35}O_{10}N_6)_2Zn$, have been prepared. Amphopeptone has $[\alpha]_D - 27{\cdot}24$. Molecular weight determinations by Beckmann's method confirmed the formulæ quoted. By the action of fuming hydrochloric acid on amphopeptone, lysine and arginine (?) were obtained together with tyrosine. E. W. W.

Organic Chemistry.

Action of Nitrous Acid on Propylene; Propylene Nitrosite. By NICOLAUS I. DEMJANOFF (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 275—279).—By passing nitrogen trioxide, prepared from nitric acid and arsenic trioxide, through an ethereal solution of propylene, *propylene nitrosite*, $C_3H_6O_3N_2$, is obtained; it crystallises from ethyl acetate in shining, white prisms which melt and evolve gas at 119—120°. On reduction with tin and hydrochloric acid, it is converted into propylenediamine.

From this and earlier results, the author concludes that when acted on by nitrous acid, hydrocarbons of the types $R\cdot CH:CH_2$ and $R\cdot CH:CH\cdot R$ yield nitrosites of the formula $C_nH_{2n}N_2O_3$, whilst hydrocarbons having the constitution $R_2:C:CH\cdot R$ or $R_2:C:C:R_2$ give nitrosates of the composition $C_nH_{2n}N_2O_4$. T. H. P.

Propylhexamethylene. By NICOLAI KURSANOFF (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 410—412; *Ber.*, 1901, **34**, 2035—2036).—Propylhexamethylene, obtained together with hexanaphthylene and an unsaturated hydrocarbon of higher boiling point when zinc propiodide acts on chlorohexamethylene, boils at 155—156° under 730 mm. pressure; Sabatier and Senderens (this vol., i, 263) gave 153—154°. It has a sp. gr. 0·7996 at 0°/0° and 0·7865 at 20°/0°. It exhibits all the properties of the naphthenes and is slowly dissolved in nitric acid of sp. gr. 1·53, whilst with bromine in presence of aluminium bromide it yields an oily bromide. T. H. P.

Action of Cuprous Salts on Hydrocarbons and Carbon Monoxide. By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1901, [vii], **23**, 32—39).—A hydrochloric acid solution of cuprous chloride containing its constituents in the proportions corresponding with the formula $CuCl,3\cdot42HCl,17\cdot5H_2O$, when maintained for 8 days in contact with carbon monoxide under the ordinary pressure and at a temperature of 8°, absorbs about 50 times its volume of the gas, the relation between the two reagents being expressed molecularly in the following manner, $CuCl,0\cdot87CO$. On examining the product, it is found that the gas exists partly in solution and partly in the crystallised compound, $2CuCl,CO,H_2O$.

The maximum absorption of acetylene effected under similar conditions by a cuprous chloride solution of the concentration indicated, agrees with the relationship $3CuCl,C_2H_2$; in the case of ethylene, the ratio is $CuCl,0\cdot17C_2H_4$. The absorption of propylene by the cuprous solution is very slow at the commencement, but goes on increasing until after 63 days the ratio is $CuCl,0\cdot25C_3H_6$. A similar reaction is observed in the case of trimethylene, the ratio after 63 days being $CuCl,0\cdot33C_3H_6$. An excess of trimethylene, when maintained in contact with the cuprous chloride, is partly dissolved and partly converted into propylene. The action of cuprous chloride on propylene and trimethylene does not end with the formation of substances corresponding with the compound $2CuCl,CO$, and dissociating when subjected to changes of pressure or temperature. The cuprous liquid containing either of the two hydrocarbons does not evolve any gas when diluted or boiled; it seems to contain some ethereal product united with the copper salt. G. T. M.

Action of Acetylene on Cuprous Chloride dissolved in a neutral solution of Potassium Chloride. By R. CHAVASTELON (*Compt. rend.*, 1901, 132, 1489—1492. Compare Abstr., 1900, i, 470).—When a current of acetylene plays over the surface of a saturated solution of cuprous and potassium chlorides, a purple precipitate is produced consisting of the compound C_2H_2,Cu_2Cl_2,Cu_2O, and the solution becomes acid. On passing the gas into the liquid and thoroughly agitating the mixture, the purple precipitate becomes rapidly converted into the yellow crystals, $C_2H_2[(Cu_2Cl_2)_2,KCl]_2$. When the solutions are diluted, the purple precipitate is produced whether the mixture is agitated or not. G. T. M.

Acetylenoid Metallic Radicles. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1901, 132, 1525—1527).—Recent experiments confirm the view that the acetylides C_2M_2 and C_2MH correspond with the sulphides SM_2 and SMH, and the metallic ammonia derivatives NM_3, NM_2H, and NMH_2. Many of the compounds of the acetylides may be regarded as containing a radicle of the type C_2R_3, this group being analogous to the substituted ammonium radicle NR_4. The simple and double nitrates, sulphates, chlorides, and iodides of silver acetylide may be considered to contain the radicle C_2Ag_3, whilst the cuprous salts have the groups C_2Cu_3, C_2HCu_2, and C_2H_2Cu. The double iodide may be written C_2Cu_3I,CuI, and Chavastelon's compounds (compare Abstr., 1900, ii, 470, and preceding abstract) may be formulated in the following manner, $(C_2H_2Cu)Cl,CuCl$, or C_2HCu_2Cl,HCl, and $(C_2Cu_3)Cl,CuCl,H_2O$, or $(C_2Cu_3)CuCl_2,H_2O$, this compound corresponding with the author's salts $(C_2Ag_3)Cl,AgCl$ and $(C_2Cu_3)I,CuI$ (Abstr., 1900, i, 324). The more complex derivatives studied by Chavastelon may be similarly represented. G. T. M.

Action of Nitric Acid on Acetylene. By GIUSEPPE TESTONI and L. MASCARELLI (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 442—444. Compare Baschieri, Abstr., 1900, i, 534).—By passing acetylene into nitric acid of sp. gr. 1·52 in a flask immersed in water until the acid assumes a dark green colour, and then gradually pouring it into a large volume of cold water, besides nitroform and the neutral substance, $C_6H_4O_3N_4$, obtained by Baschieri (*loc. cit.*), the following compounds are formed:

(1) A straw-yellow, explosive *substance* melting at 78° without decomposition; when crystallised from benzene or light petroleum, copious evolution of nitrous fumes occurs, and transparent, colourless crystals of a neutral *compound*, $C_4H_2O_3N_4$, melting at 108°, separate; this compound, which has the normal molecular weight in acetic acid or benzene, can be crystallised unchanged from boiling water and is readily soluble in the organic solvents.

(2) A monobasic *acid*, $C_4H_3O_3N$, separating from toluene in large, faintly yellowish crystals melting at 149°; it dissolves readily in

alkalis and in the ordinary solvents, and has the normal molecular weight in freezing acetic acid, whilst its aqueous solution has a strong acid reaction and can be titrated with potassium hydroxide. It forms a stable *silver* salt which forms a yellowish, curdy precipitate melting and decomposing with a slight explosion at about 165°. T. H. P.

Propyl-ψ-nitrole and *s*-Tetramethyldinitroazoxymethane. By A. SCHÖFER (*Ber.*, 1901, **34**, 1910—1914).—Propyl-ψ-nitrole, which is best prepared by the action of an aqueous solution of nitrous acid on acetoxime, yields acetoxime when treated with alcoholic sodium hydroxide or when reduced by means of aluminium amalgam. The nitrole, when treated with aniline or benzylamine, yields diazoaminobenzene or benzaldehyde respectively. *s*-Tetramethyldinitroazoxymethane boils at about 100° under 25 mm. pressure with slight decomposition, is only reduced by zinc dust and acetic acid, is not changed by potassium hydroxide or fuming nitric acid, but is decomposed by bromine and by concentrated sulphuric and hydrochloric acids. R. H. P.

Etherification by Means of Inorganic Salts. By GIUSEPPE ODDO (*Gazzetta*, 1901, **31**, i, 285—374).—The author gives first a historical account of the etherification of alcohol, and then the conclusions drawn from a large number of experiments on etherification by inorganic salts. He finds that the degree of readiness with which alcohols are etherified increases with their molecular weight, and is also influenced by the presence in the molecule of a side chain in a neighbouring position to the hydroxyl group; the collateral chains render the hydroxyl less readily mobile, and when this group is removed by a more or less energetic reagent, there is a tendency for the tension holding together the atoms in the molecule to be released and further breaking down to occur. Thus *iso*butyl alcohol, when treated at 200° with anhydrous copper sulphate, yields *iso*butyl ether together with a little *iso*butane, whilst with ferric chloride or stannous sulphate it gives only di*iso*butene. A similar influence is exerted on the hydrogen atom of the CH group in *iso*amyl alcohol, which, with the last-named salt, yields dimethylallene.

The fatty alcohols used by the author were methyl, ethyl, propyl, *n*-butyl, *iso*butyl, *iso*amyl, *n*-heptyl, *n*-octyl, and cetyl; it is found that all the saturated, primary, aliphatic alcohols are etherified at 200° by some of the salts of the heavy metals, and often by very small proportions of these salts.

The etherifying action of a large number of compounds on benzyl and cumyl alcohols was investigated, the main bulk of the author's experiments being made with these two alcohols. None of the inorganic oxides and hydroxides having a basic character (sodium, calcium, and zinc oxides, potassium, ferric, and stannous hydroxides) have any etherifying action on these alcohols even on long boiling; antimony and arsenic trioxides act slowly and to some extent as reducers, whilst phosphoric oxide etherifies them very rapidly even when traces of it only are present; the chlorides of the alkali and alkaline earth metals are quite inactive, whilst nickel chloride and zinc iodide tend to bring about more complex condensations, and silver chloride etherifies cumyl alcohol readily, but is without action on benzyl alcohol; of the other chlorides, that of magnesium has but a slight action, those of cobalt, cadmium and iodine, and mercuric and mercurous chlorides act slowly, but give good yields of ether, whilst the chlorides of copper, aluminium, and antimony and sulphur monochloride act still better, and stannous, stannic, ferric, and zinc chlorides give the best results. Hydrochloric acid and alkyl chlorides etherify but slowly, whilst sulphuric acid, even traces of it, acts very rapidly. The sulphates show actions similar to those of the corresponding chlorides. In the aromatic, as in the aliphatic series, the degree of readiness with which the alcohols undergo etherification increases with the molecular weight, and for alcohols containing an equal number of carbon atoms in the molecule, one belonging to the aromatic series is more readily etherified than one of the aliphatic series.

The results of the author's measurements lead to the conclusion that the power to cause etherification of the primary saturated alcohols is possessed by salts of the heavy metals and of magnesium formed with energetic acids, and this is more especially the case with those tending to form basic salts. At the temperature of 200°, all the normal salts of the alkali and alkaline-earth metals are inactive, as are also their oxides, basic hydroxides, and carbonates.

The author finds further that along with the increasing readiness of the alcohols to etherify as the molecular weight and the complexity of the space formula of the alcohol increase, there is a corresponding diminution in the stability of the ether formed.

After discussing the various hypotheses which have from time to time been put forward to explain the mechanism of etherification, the author gives his own views on the subject. In the case of ferric chloride, for example, he considers the action on alcohol to consist of the replacement of the chlorine atoms by radicles, $\cdot O\cdot CH_2R$, hydrogen chloride being evolved, and the compounds $FeCl_2\cdot O\cdot CH_2R$, $FeCl(O\cdot CH_2R)_2$, and $Fe(O\cdot CH_2R)_3$, being formed; the hydrogen chloride may, under favourable conditions, react with the alcohol, yielding an alkyl chloride, which with the above compounds gives ferric chloride and the ether corresponding with the alcohol, thus:

$$\begin{aligned} FeCl_2\cdot O\cdot CH_2R &+ CH_2RCl = FeCl_3 + (RCH_2)_2O. \\ FeCl(O\cdot CH_2R)_2 &+ 2CH_2RCl = FeCl_3 + 2(RCH_2)O. \\ Fe(O\cdot CH_2R)_3 &+ 3CH_2RCl = FeCl_3 + 3(RCH_2)O. \end{aligned}$$

These views are supported by the fact that in all the cases examined the formation of hydrogen chloride and alkyl chloride was observed; the metallic alkoxides are unstable and difficult to isolate, but their existence is indicated by the formation of benzyl ethyl ether when benzyl alcohol is treated with ferric chloride and ethyl iodide. Similar explanations hold for the etherification produced by other salts.

The experimental results are given in detail. T. H. P.

Contact Action and the Secondary and Tertiary Alcohols. By AUGUSTE TRILLAT (*Compt. rend.*, 1901, 132, 1495—1497. Compare this vol., i, 441).—The vapour of *iso*propyl alcohol, when mixed with air and passed over a heated platinum spiral, undergoes oxidation, the yield of acetone being 16 per cent. *sec.*Butyl alcohol, when similarly treated, yielded a small quantity of methyl ethyl ketone, whilst *sec.*octyl alcohol (methylhexylcarbinol) gave rise to methyl hexyl ketone; *sec.*amyl alcohol furnished traces of a ketonic compound which was not identified.

*tert.*Butyl alcohol under these conditions is oxidised, yielding acetone and formaldehyde. Since acetone itself, when oxidised by oxygen in contact with the heated spiral, yields formaldehyde, this product, in the preceding example, may be derived either directly from the alcohol, $CMe_3{\cdot}OH + 2O = COMe_2 + CH_2O + H_2O$, or by a secondary oxidation of the ketone. The amount of acid produced is negligible.

*tert.*Amyl alcohol, $CMe_2Et{\cdot}OH$, behaves similarly, also giving rise to acetone and formaldehyde. G. T. M.

Active Erythritols. By Léon Maquenne and Gabriel Bertrand (*Compt. rend.*, 1901, **132**, 1419—1421).—The active erythritols (Abstr., 1900, ii, 423, 424, 472) are identical in crystalline form, and show faces of the hexagonal prism e^2, and of the rhombohedron p without any trace of hemihedrism. Both are negatively uniaxial. *d*-Erythritol [1 : 0·48005 ; pp = 130°20′, pe^2 = 119°4′], *l*-erythritol [1 : 0·47820 ; pp = 130°30′, pe^2 = 119°].

In both cases, the rotatory power in alcoholic solution is opposite in sign to the rotatory power in aqueous solution. *l*-Erythritol in water has $[\alpha]_D$ +4°·33, in alcohol of 90° $[\alpha]_D$ −10°·5 and in alcohol of 95°, −11°·50, whilst for *d*-erythritol the corresponding values are −4°·40, +10°·10, and +11°·10.

The tetracetins of the active erythritols are syrupy and non-crystallisable; when dissolved in chloroform, the values of $[\alpha]_D$ are +21°·6 and −19°·28 respectively. The dibenzoic acetals crystallise in slender, white needles melting at 231° and subliming slowly even at 200°. The divaleric acetals crystallise in nacreous plates melting at 105—106°.

When oxidised with nitric acid, *d*-erythritol yields ordinary tartaric acid, whilst *l*-erythritol yields a tartaric acid with equal optical activity of opposite sign. All the active compounds described above yield racemic modifications. C. H. B.

Racemic Erythritol. By Léon Maquenne and Gabriel Bertrand (*Compt. rend.*, 1901, **132**, 1565—1567).—The authors, being in possession of a stereoisomeric pair of erythritols, have synthesised the racemic compound formerly obtained by Griner from the stereoisomeric crotonylene dibromides (Abstr., 1893, i, 450; 1894, i, 62). The inactive substance is more soluble than its components; it is probably a pseudoracemic compound, and may be caused to separate from its saturated solutions by the addition of traces of either of the active forms.

The properties of the tetracetyl, dibenzylidene and diheptylidene derivatives of the authors' racemic compound agree entirely with those of the corresponding compounds prepared by Griner. G. T. M.

Constitution of mixed Carbonic Esters of Alcohols and Phenols. By Paul Cazeneuve (*Bull. Soc. Chim.*, 1901, [iii], **25**, 632—636).—An attempt to show that the two hydroxyl groups of carbonic acid are not identical in function, one being acidic and the other alcoholic. T. M. L.

Optical Activity of Lecithin. II. By C. ULPIANI (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 421—425. Compare this vol., i, 491).—Lecithin cadmiochloride, prepared as previously described (*loc. cit.*), gives on analysis results agreeing well with numbers for a lecithin containing either two stearic acid residues or two oleic acid residues. On decomposing the compound with barium hydroxide and treating the soap formed with hydrochloric acid, a mixture of stearic and oleic acids is obtained. Whether both the acids occur in the same lecithin molecule or whether several lecithins exist containing different fatty acids is as yet uncertain. T. H. P.

Calcium Glyceroarsenate. By CAMILLE PAGEL (*J. Pharm.*, [vi], 13, 449—452).—With the view of administering arsenic in a form analogous to glycerophosphoric acid, the author has prepared calcium glyceroarsenate, $C_3H_5(OH)_2 \cdot O \cdot AsO_3Ca,2H_2O$, by heating a mixture of glycerol and arsenic acid for several days, then neutralising with milk of lime, filtering, evaporating, and precipitating with 95 per cent. alcohol. The dried product is a powder, insoluble in water and in alcohol, but readily soluble in mineral and organic acids, and especially in a weak solution of citric acid. The arsenic which it contains cannot be detected by ammonium molybdate or by hydrogen sulphide. M. J. S.

Manganic Acetate. By ODIN T. CHRISTENSEN (*Zeit. anorg. Chem.*, 1901, 27, 321—340).—See this vol., ii, 512.

Dry Distillation of the Salts of Fatty Acids. By WALTHER DILTHEY (*Ber.*, 1901, 34, 2115—2125).—Calcium valerate (900 grams) yields on dry distillation an oily distillate (287 grams) consisting of a mixture of ketones and aldehydes, accompanied by a gaseous product which, when passed through bromine, gives rise to 323 grams of olefine dibromides, the residual gas consisting of carbon monoxide, methane, ethane, and hydrogen. The olefines consist chiefly of the butylenes, accompanied by smaller quantities of ethylene, propylene, and traces of the higher homologues; these hydrocarbons were identified by an examination of their bromine and iodine derivatives. The mixture of aldehydes and ketones contains the following compounds: Valeraldehyde, valerone, methyl *iso*butyl ketone, the ketone $C_7H_{14}O$, probably a methyl amyl ketone, an isomeride of valerone, and notable quantities of the higher ketones. The unsaturated aldehyde, *α-iso*propyl-*β-iso*butylacraldehyde, could not be detected amongst the products of distillation; this substance, when present in a mixture, is readily identified by means of its condensation *product*, $C_{17}H_{25}O_7N_7$, with aminoguanidine, this derivative crystallising from alcohol in yellow needles.

On dry distillation, a mixture of potassium *iso*valerate and sodium acetate yields carbon monoxide, hydrogen, methane, butylene, *iso*propyl alcohol, and a mixture of ketones consisting chiefly of methyl *iso*butyl ketone. G. T. M.

Preparation of Acid Anhydrides by the aid of Tertiary Amines. By EDGAR WEDEKIND (*Ber.*, 1901, 34, 2070—2077).—The acid chlorides react with tertiary amines, forming the hydrochloride of the amine and the acid anhydride, if sufficient water be present in the mixture. In some cases, the anhydride can be obtained by mixing the acid chloride and amine, filtering from the hydrochloride which separates out, and then adding the requisite amount of water to the filtrate, which probably contains an unstable intermediate product of the type $CR_2{:}CO$. *iso*Butyric anhydride is readily formed when the corresponding chloride is mixed with pyridine in ethereal solution, the pyridine hydrochloride filtered off, and cold water added, and *iso*valeric anhydride can be prepared in a similar manner. α-Bromopropionic anhydride and α-bromo*iso*butyric anhydride can also be prepared by treating the chlorides with pyridine in ethereal solution and pouring the mixture on to ice. Cinnamic anhydride is best prepared by mixing the chloride with pyridine and treating the compact mass with warm water. Phenylacetic chloride also reacts in a similar manner, but the anhydride is not always produced, the reaction being evidently a complicated one; diphenylacetone is always obtained in the reaction, and is probably formed by the decomposition of pyridine phenylacetate on distillation.

Diphenylacetonesemicarbazone crystallises in pointed needles or silvery plates melting at 145—146°. A. H.

Action of Iodine on the Silver Salts of Hydroxy-acids. By R. O. HERZOG and R. LEISER (*Monatsh.*, 1901, 22, 357—360).—The reaction of the silver salts of α-hydroxy-acids with iodine are represented thus:

$$2R{\cdot}CH(OH){\cdot}CO_2Ag + I_2 = 2AgI + CO_2 + R{\cdot}CH(OH){\cdot}CO_2H + R{\cdot}CHO.$$
$$2CR_2(OH){\cdot}CO_2Ag + I_2 = 2AgI + CO_2 + R{\cdot}C(OH){\cdot}CO_2H + COR_2.$$

Lactic acid yields aldehyde; glycollic acid, formaldehyde; mandelic acid, benzaldehyde, and α-hydroxy*iso*butyric acid, acetone. In all cases, the reaction takes place with ease, and the aldehyde or ketone is readily isolated. From glyceric acid (αβ-dihydroxypropionic acid) glycolaldehyde is not obtained, but formaldehyde. K. J. P. O.

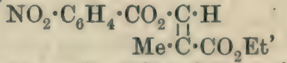
Production of Methylsuccinic Acid from Pyruvic Acid. By LUDWIG WOLFF (*Annalen*, 1901, 317, 22—26. Compare this vol., i, 502).—Pyruvic acid, after purification by repeated distillation under 15 mm. pressure, yields only traces of methylsuccinic acid when heated to its boiling point under atmospheric pressure, but when treated with hot concentrated hydrochloric acid, a notable quantity of the dibasic acid is produced; a yield of 60 per cent. is obtained when the ketonic acid is first converted into α-ketovalerolactone-γ-carboxylic acid, the intermediate compound being heated with the mineral acid for 1 hour at 120°. A smaller yield is obtained on heating the intermediate product with water at 120°; pyruvic acid itself, under these conditions, does not give rise to any methylsuccinic acid. G. T. M.

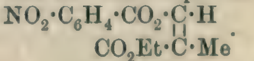
α-Hydroxy-β-butenoic Acid (Vinylglycollic Acid) and its Decompositions. By G. VAN DER SLEEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 4, 79—83).—The nitrile of α-hydroxy-β-butenoic acid boils at 93—94° under 16—17 mm. pressure, and forms an *acetate* when treated with acetic anhydride. Both the nitrile and its acetate are converted into the *amide* of *α-hydroxy-β-butenoic acid* by the action of concentrated hydrochloric acid; this melts at 80·8° and when hydrolysed yields the *acid*, which crystallises in needles, boils at 125—130° under 12—13 mm. pressure, has a dissociation constant 0·046, and forms an *ethyl* ester boiling at 173° under 756·5 mm. pressure. The *dibromo-amide* does not melt, but chars when heated; the *dibromo-acid* melts at 121—121·5° and yields α-hydroxybutyric acid when reduced with sodium amalgam. α-Hydroxybutenoic acid when treated with strong acids, yields propionylformic acid, which melts at 31·5—32°, boils at 73—75° under 15 mm. pressure, and forms a *phenylhydrazone* melting at 143—144°, and an *oxime* melting and decomposing at 154°; *ethyl propionylformate* boils at 66—67° under 16 mm. pressure, and forms a *phenylhydrazone* melting at 191°. When α-hydroxybutenoic acid is treated with alkalis, a crystalline *acid* (probably 2-*hydroxy-*Δ^3*-tetrahydrophthalic acid*) is formed; it melts at 142—142·5°, and loses a mol. of carbon dioxide forming a syrupy *acid* (probably *o*-ketohexahydrobenzoic acid), which forms a *phenylhydrazone* melting at 159°, an *oxime* decomposing at about 177°, and by further elimination of carbon dioxide yields an oil (probably *cyclo*hexanone). R. H. P.

Geometrically Isomeric Derivatives of Ethereal Formylpropionates. By Wilhelm Wislicenus and Charles L. Wolff (*Annalen*, 1901, **316**, 333—336. Compare Abstr., 1900, i, 597, and this vol., i, 361).

—Ethyl formylpropionate resembles ethyl formylacetate in yielding two isomeric p-*nitrobenzoates* when its sodium derivative is treated with *p*-nitrobenzoic chloride.

The α-compound is obtained when the condensation is effected in cold dry ether free from alcohol; it crystallises from alcohol and melts at 120—121°. The β-compound is produced either by heating its isomeride at 240—250° in sealed tubes, or by the direct action of *p*-nitrobenzoic chloride on the sodium derivative of ethyl formylpropionate dissolved in a dilute aqueous sodium hydroxide solution; it crystallises from alcohol, melts at 140—142°, and can be heated to 250° without undergoing any change.

The configuration  $\begin{array}{r}NO_2\cdot C_6H_4\cdot CO_2\cdot C\cdot H\\ \|\;\;\;\;\;\;\;\;\\ Me\cdot C\cdot CO_2Et\end{array}$, in which the acidic groups are arranged on opposite sides of the ethylenoid carbon atoms, is ascribed to the more stable β-derivative, the labile α-isomeride having in all probability the structure represented by



$$\begin{array}{r}NO_2\cdot C_6H_4\cdot CO_2\cdot C\cdot H\\ \|\;\;\;\;\;\;\\ CO_2Et\cdot C\cdot Me\end{array}.$$

G. T. M.

Nitration of Ethereal Acetoacetates and their Acyl Derivatives. By Louis Bouveault and A. Bongert (*Compt. rend.*, 1901, **132**, 1569—1572. Compare this vol., i, 311).

—The two isomeric methyl butyrylacetoacetates yield on nitration the *compound* $(C_3H_2O_3N)_2$; this substance is an oil boiling at 151° under 10 mm. pressure and having a sp. gr. 1·429 at 0°/4°; its molecular weight was determined by the cryoscopic method in benzene. On treatment with aqueous ammonia solution, the preceding ester is transformed into an *amide*, $C_4H_4O_4N_4$, melting at 253°.

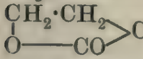
Ethyl diacetylacetate when nitrated yields an *ethyl ester* boiling at 161° under 10 mm. pressure, and having a sp. gr. 1·296 at 4°/0°; this compound on treatment with ammonia yields the amide melting at 253°. The new ethyl ester is also produced by nitrating ethyl acetoacetate; it is also a by-product in the preparation of ethyl nitroacetate (Abstr., 1900, i, 5). These results are most readily explained by assuming the formation of the nitro-ester, $NO_2\cdot CHAc\cdot CO_2Me$, during the nitration of methyl acetoacetate; by hydrolysis, this product would give rise to methyl nitroacetate, $NO_2\cdot CH_2\cdot CO_2Me$, which, under the influence of mineral acids, undergoes condensation with the elimination of water, $2NO_2\cdot CH_2\cdot CO_2Me = 2H_2O + C_6H_6O_6N_2$.

G. T. M.

Synthesis of αβγ-Trihydroxybutyric Acid [Erythric Acid]. By C. Prey (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, 4, 77—78).—αβγ-Trihydroxybutyric acid has been synthesised by treating the amide of α-hydroxybutenoic acid (compare this vol., i, 499) with an alkaline solution of potassium permanganate. Various halogen compounds of the type $CH_2X\cdot CHX\cdot CH(OH)\cdot CONH_2$ were prepared, but none gave erythric acid when hydrolysed.

R. H. P.

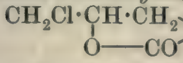
Behaviour of Alkylene Oxides towards Ethyl Malonate and Ethyl Acetoacetate. By Wilhelm Traube and Erich Lehmann (*Ber.*, 1901, 34, 1971—1983. Compare Abstr., 1899, i, 417).—*Ethyl butyrolactonecarboxylate* [*lactone* of *ethyl γ-hydroxyethylmalonate*],

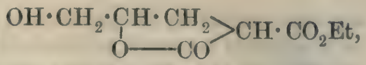


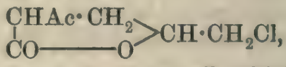
$\begin{matrix}CH_2\cdot CH_2\\ O\text{——}CO\end{matrix}>CH\cdot CO_2Et$, prepared by the action of epichlorohydrin on ethyl sodiomalonate, which was previously (*loc. cit.*) converted directly into the amide, has now been isolated as a colourless, odourless oil which boils at 175° under 25 mm. pressure; the *silver* salt has also been prepared from the amide by hydrolysing with sodium hydroxide and precipitating with silver nitrate.

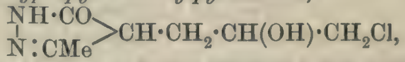
At moderately low temperatures, epichlorohydrin interacts with ethyl sodiomalonate and ethyl sodioacetoacetate in the same manner as ethylene oxide; the first product is probably a chlorohydroxypropyl derivative, but this is at once converted into a lactone by loss of a molecule of alcohol; at higher temperatures, condensation takes place with elimination of sodium chloride, and a similar interaction takes place in the case of ethyl methyl- and ethyl-acetoacetates.

Ethyl δ-chloro-γ-valerolactone-α-carboxylate [*lactone* of *ethyl δ-dichloro-γ-hydroxypropylmalonate*],



$\begin{matrix}CH_2Cl\cdot CH\cdot CH_2\\ O\text{——}CO\end{matrix}>CH\cdot CO_2Et$, prepared from epichlorohydrin and ethyl malonate below 50°, is an oil of sp. gr. 1·274 at 15° which boils at 181° under 12 mm. pressure; the *sodium* salt crystallises from absolute alcohol, and melts and decomposes at 172°; the diamide has already been described (*loc. cit.*); the *hydrazido*-ester, $C_8H_{15}O_4N_2Cl$, crystallises from alcohol and melts at 129°. *Ethyl* *δ-hydroxy-γ-valerolactone-α-carboxylate,*  $\begin{array}{l}OH\cdot CH_2\cdot \overset{}{C}H\cdot CH_2\\ \qquad O\text{——}CO\end{array}\!\!>CH\cdot CO_2Et$, prepared by the action of alcoholic sodium hydroxide on the chloro-ester, is a colourless syrup which decomposes at about 200° when distilled in a vacuum. *γδ-Dihydroxypropylmalonamide,* $OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot CH(CO\cdot NH_2)_2$, prepared by the action of alcoholic ammonia on the preceding compound, crystallises from dilute alcohol and melts at 140·5°. *Ethyl dichloro-γ-valerolactone-α-carboxylate,* $C_8H_{10}O_4Cl_2$, prepared by the action of chlorine on the chloro-ester, crystallises from absolute alcohol and melts at 55°; the *bromochloro-ester,* $C_8H_{10}O_4ClBr$, is an oil which distils at 180° under 12 mm. pressure.

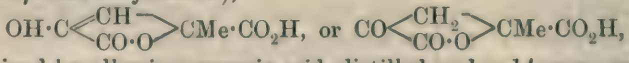
δ-Chloro-α-acetyl-γ-valerolactone,  $\begin{array}{l}CHAc\cdot CH_2\\ CO\text{———}O\end{array}\!\!>CH\cdot CH_2Cl$, prepared from epichlorohydrin and ethyl acetoacetate, is an oil which boils at 163° under 12 mm. pressure. Hydrazine hydrate converts it into *4-γ-chloro-β-hydroxypropyl-3-methylpyrazolone,*


$$\begin{array}{l}NH\cdot CO\\ N:CMe\end{array}\!\!>CH\cdot CH_2\cdot CH(OH)\cdot CH_2Cl,$$

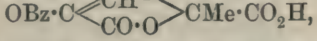
which crystallises in needles from absolute alcohol and melts at 150·5°. *Methyl γδ-dihydroxybutyl ketone,* $OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot COMe$, prepared by warming the lactone with aqueous potassium carbonate, is an oil which is miscible with water and boils at 189—190° under 20 mm. pressure; it combines with 2 mols. of phenylcyanate to a *phenylcarbamate,* $C_{20}H_{22}O_5N_2$, which crystallises from alcohol and melts at 136°; sodium amalgam converts the ketone into *αβε-hexanetriol,* $OH\cdot CH_2\cdot CH(OH)\cdot [CH_2]_2\cdot CHMe\cdot OH$, which is a sweet syrup miscible with water, and distilling at 178° under 12 mm. pressure.

The product of the action of epichlorohydrin on ethyl sodiomethylacetoacetate is an oil which boils at 202° under 25 mm. pressure, and is probably acetylethoxymethyl-γ-valerolactone; ethyl ethylacetoacetate gives an oil boiling at 210° under 25 mm. pressure, which is probably acetylethoxyethyl-γ-valerolactone. T. M. L.

New Condensation Product from Pyruvic Acid. By Ludwig Wolff (*Annalen,* 1901, **317**, 1—22. Compare Abstr., 1899, i, 483, 514; and de Jong, this vol., i, 446).—[With Willy Herold.]—α-Ketovalerolactone-γ-carboxylic acid, (γ-lactone of α-keto-γ-hydroxybutane-αγ-dicarboxylic acid),


$$OH\cdot C\!\!<\!\begin{array}{l}CH\\ CO\cdot O\end{array}\!\!>CMe\cdot CO_2H, \text{ or } CO\!\!<\!\begin{array}{l}CH_2\\ CO\cdot O\end{array}\!\!>CMe\cdot CO_2H,$$

is obtained by allowing pyruvic acid, distilled under 14 mm. pressure, to remain at the ordinary temperature for some weeks and then evaporating under diminished pressure over quicklime; it crystallises from a mixture of ether and benzene in white plates or prisms melting at 116—117°. The acid is hygroscopic and readily dissolves in water, alcohol, or ether, being, however, sparingly soluble in chloroform, benzene, or light petroleum; its aqueous solution reduces Fehling's solution and ammoniacal silver nitrate, develops a red coloration with ferric chloride, and when titrated with sodium hydroxide in cold solutions with phenolphthalein as indicator gives numbers corresponding with those for a dibasic acid. In alkaline solutions, the acid is readily reconverted into pyruvic acid. On treating a solution of the compound with lead acetate, a yellow *lead* salt is precipitated having the composition $C_6H_4O_5Pb,3H_2O$; this substance does not appear to be an immediate derivative of the original ketonic acid, for the acid regenerated from the lead compound gives a phenylhydrazone melting at 182°, whilst the *phenylhydrazone* of α-ketovalerolactone-γ-carboxylic acid obtained by mixing its generators in aqueous solution crystallises from this solvent in yellow needles melting at 197—198°. The latter phenylhydrazone, when boiled with sodium hydroxide solution, yields a dibasic *γ-hydroxy-acid*, $C_{12}H_{14}N_2O_5,2H_2O$, crystallising in pale yellow needles and melting at 165°. The original ketonic acid, when subjected to the Schotten-Baumann reaction, yields a *benzoyl* derivative,

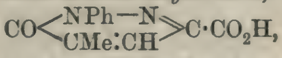


$$\mathrm{OBz\cdot C}{<}\begin{matrix}\mathrm{CH}-\!-\\ \mathrm{CO\cdot O}\end{matrix}{>}\mathrm{CMe\cdot CO_2H},$$

melting at 118° and developing no coloration with ferric chloride; titration with sodium hydroxide and phenolphthalein indicates that this product is a monobasic acid.

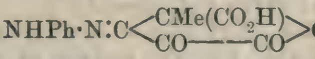
α-isoNitrosovalerolactone-γ-carboxylic acid results from the action of hydroxylamine hydrochloride on the ketonic acid; it crystallises from water in lustrous prisms containing $1H_2O$, and melts at 118—119°. The *iso*nitroso-compound does not regenerate hydroxylamine with sodium hydroxide, and develops no coloration with ferric chloride.

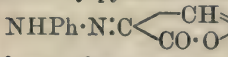
1-*Phenyl-5-methylpyridazone-3-carboxylic acid*,

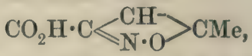


$$\mathrm{CO}{<}\begin{matrix}\mathrm{NPh-N}\\ \mathrm{CMe{:}CH}\end{matrix}{>}\mathrm{C\cdot CO_2H},$$

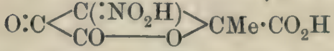
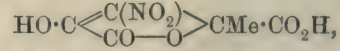
produced from the γ-hydroxy-acid by heating this substance either alone or with dilute hydrochloric acid, may also be prepared by boiling the phenylhydrazone (m. p. 198°) with sodium hydroxide solution, and treating the product with hot 20 per cent. hydrochloric acid; it melts at 213—214° and readily dissolves in alcohol, being sparingly soluble in ether, benzene, or water. 1-*Phenyl-5-methylpyridazone*, obtained as a by-product in the preceding condensation, crystallises in prisms and melts at 89—90°; it is isomeric with Ach's 1-phenyl-3-methylpyridazone (Abstr., 1890, i, 71), and like this base gives, after reduction with sodium and alcohol, a red coloration with an acid solution of potassium dichromate.

The *β-phenylhydrazone*,  $\mathrm{NHPh\cdot N{:}C}{<}\begin{matrix}\mathrm{CMe(CO_2H)}\\ \mathrm{CO-\!-\!-CO}\end{matrix}{>}\mathrm{O}$, of diketovalerolactone-γ-carboxylic acid, produced by the action of benzenediazonium chloride on a sodium carbonate solution of the ketonic acid, crystallises from glacial acetic acid in brick-red needles and melts at 188°; it is somewhat sparingly soluble in ether, chloroform, or benzene; its solution in concentrated sulphuric acid develops a deep blue coloration with potassium dichromate.

β-Bromo-α-ketovalerolactone-γ-carboxylic acid, prepared by brominating the ketonic acid in chloroform solution, crystallises from ether and chloroform in white prisms decomposing at 149°; it is a dibasic acid and develops a red coloration with ferric chloride. When this bromo-acid is treated in aqueous solutions with phenylhydrazine hydrochloride, two isomeric phenylhydrazones are obtained, together with 1-phenyl-5-methylpyrazole-3-carboxylic acid (m. p. 134°). The *phenylhydrazone*,  $\mathrm{NHPh{\cdot}N{:}C}<\begin{smallmatrix}\mathrm{CH}\\ \mathrm{CO{\cdot}O}\end{smallmatrix}>\mathrm{CMe}$, of α-ketoangelicalactone separates first from the product of reaction and crystallises from alcohol in yellowish-red needles melting at 128—129°; at this temperature, it is converted into its *isomeride*, $\mathrm{NHPh{\cdot}N{:}C}<\begin{smallmatrix}\mathrm{CH_2}\\ \mathrm{CO{\cdot}O}\end{smallmatrix}>\mathrm{C{:}CH_2}$; this substance, which is also produced in the preceding reaction, crystallises in pale yellow needles and melts at 177°. Both isomerides, on boiling in alkaline solution, yield 1-phenyl-5-methylpyrazole-3-carboxylic acid, and their solutions in concentrated sulphuric acid develop violet colorations with potassium dichromate.

3-*Methyl*iso*oxazole-5-carboxylic acid*,  $\mathrm{CO_2H{\cdot}C}<\begin{smallmatrix}\mathrm{CH}\\ \mathrm{N{\cdot}O}\end{smallmatrix}>\mathrm{CMe}$, results from the action of hydroxylamine hydrochloride on the bromo-acid, and crystallises from boiling water in white prisms or plates melting at 173—174°; the acid readily dissolves in alcohol, hot water, or sodium carbonate solution, and is monobasic.

α-*Nitroketovalerolactone-γ-carboxylic acid*,

 $\mathrm{O{:}C}<\begin{smallmatrix}\mathrm{C({:}NO_2H)}\\ \mathrm{CO{-}O}\end{smallmatrix}>\mathrm{CMe{\cdot}CO_2H}$ or  $\mathrm{HO{\cdot}C}<\begin{smallmatrix}\mathrm{C(NO_2)}\\ \mathrm{CO{-}O}\end{smallmatrix}>\mathrm{CMe{\cdot}CO_2H}$,

is produced, together with oxalic acid, by slowly adding the ketonic acid to absolute nitric acid cooled to −5°; the acid readily dissolves in water, alcohol, or ether, but is sparingly soluble in benzene, chloroform, or light petroleum; it crystallises in aggregates of white needles, and melts with decomposition at 152°. In aqueous solution, the acid gradually decomposes, yielding oxalic acid. Two mols. sodium hydroxide neutralise it in cold solution, whereas 3 mols. are required on warming. G. T. M.

Behaviour of Tertiary Bases towards Methyl Bromomalonate. By EDGAR WEDEKIND (*Ber.*, 1901, 34, 2077—2081. Compare *Zur Stereochemie des fünfwerthigen Stickstoffes, Leipzig*, 1899).—Methyl bromomalonate does not form a quaternary bromide with benzylpiperidine as does the corresponding acetic ester, but loses the elements of hydrogen bromide and yields methyl ethylenetetracarboxylate. This substance forms tabular crystals of the monoclinic system [$a:b:c = 2{\cdot}2170:1:?$; $\beta = 83{\cdot}5°$].

The corresponding ethyl ester is not isomorphous, but forms prismatic crystals of the triclinic system [$a:b:c = 0{\cdot}5237:1:1{\cdot}0854$; $\alpha = 93°18{\cdot}5'$; $\beta = 117°21{\cdot}5'$; $\gamma = 95°59{\cdot}5'$].

The methyl ester is only formed in small quantity from methyl bromomalonate in the ordinary way by the action of sodium ethoxide.

A. H.

Action of Acid Chlorides on Aldehydes in the presence of Zinc Chloride. By MARCEL DESCUDÉ (*Compt. rend.*, 1901, 132, 1567—1569).—Acetyl chloride and trioxymethylene interact energetically in the presence of zinc chloride, giving rise to acetylmethylene chlorohydrin (compare Henry, this Journ., 1873, 1117). When benzoyl chloride is employed, a compound is obtained having the molecular formula $(C_7H_6O_2)_2$; this substance seems to be a polymeride of benzoic acid. G. T. M.

New Mode of Decomposition of Bisulphite Derivatives. By PAUL FREUNDLER and L. BUNEL (*Compt. rend.*, 1901, **132**, 1338—1340).—When the bisulphite compound of *iso*valeraldehyde (1 mol.) is heated with a solution of sodium nitrite (½ mol.), the aldehyde is regenerated and nitrilosulphonic acid is produced, the latter being isolated by means of its sparingly soluble potassium salt. The yield of regenerated aldehyde is 90 per cent. of the theoretical, and is somewhat better than that obtained by the action of potassium carbonate.

The method is, however, not applicable to the case of citral, this compound not being completely regenerated from its bisulphite compound under these conditions. G. T. M.

Bromo-derivatives of Diethyl Ketone. By HERMANN PAULY (*Ber.*, 1901, **34**, 1771).—*Bromodiethyl ketone*, CHMeBr·COEt, prepared by the action of 1 mol. of bromine on diethyl ketone at about 80°, is a colourless, malodorous oil of sp. gr. 1·37 at 15°, which boils at 157—158° under 732 mm. pressure, and does not form a bisulphite compound.

s-*Dibromodiethyl ketone*, $CO(CHMeBr)_2$, prepared in a similar manner by the action of 2 mols. of bromine, has a sp. gr. 1·771 at 18°, boils at 80—81° under 12 mm. and at 193—195° under 732 mm. pressure, does not form a bisulphite compound, and, like *s*-dichloroacetone, dissolves readily in barium hydroxide solution, apparently with formation of dihydroxydiethyl ketone. T. M. L.

Cyclic Ketones. By PAVEL IW. PETRENKO-KRITSCHENKO and S. LORDKIPANIDZE (*Ber.*, 1901, **34**, 1702—1705. Compare next page).—A series of experiments on the velocity with which ketones of the aliphatic series combine with phenylhydrazine and hydroxylamine respectively to form phenylhydrazones and oximes show that the reactivity of the carbonyl group decreases as the length of the carbon chain increases (compare Menschutkin, Abstr., 1898, i, 119.) Thus, for example, acetone combines with 70 per cent. of phenylhydrazine and 82 per cent. of hydroxylamine when mol. proportions are allowed to interact under the conditions described elsewhere (next page), whilst methyl hexyl ketone combines only with 39 per cent. of the former and 70 per cent. of the latter, and diethyl ketone with 34 and 69 per cent. respectively. In cyclic ketones, such an influence is not exerted; thus ketohexamethylene will combine with 58 per cent. of phenylhydrazine and 86 per cent. of hydroxylamine, and thus closely approaches acetone in activity. Similarly, *p*-diketohexamethylene offers a marked contrast to acetonylacetone, in that it combines with 63 per cent. of phenylhydrazine and 88 per cent. of hydroxylamine, whilst the latter combines with 22 per cent. of phenylhydrazine and 60 per cent. of hydroxylamine under the same conditions. The authors discuss the results on stereochemical grounds, and consider that the cyclic configuration has a more marked influence on the chemical character of compounds than is generally supposed. K. J. P. O.

Conversion of αβ-Unsaturated Diketones into α-Diketones. By HERMANN PAULY and HANS VON BERG (*Ber.*, 1901, **34**, 2092—2093).—Ethylideneacetone can be converted into acetylpropionyl [methyl ethyl diketone], $CH_2Me{\cdot}CO{\cdot}COMe$, by a method similar to that employed by Pauly and Lieck (Abstr., 1900, i, 274) for the conversion of mesityl oxide into acetyl*iso*butyryl. For this purpose, the unstable *ethylideneacetone dibromide*, $CHMeBr{\cdot}CHBr{\cdot}COMe$, is converted by alcoholic potash into *bromoethylideneacetone*, $CHMe{:}CBr{\cdot}COMe$, which boils at 68° under 16 mm. pressure; this is then treated with potassium acetate, and the resulting crude *acetoxyethylideneacetone*, $CHMe{:}C(OAc){\cdot}COMe$, at once hydrolysed with dilute sulphuric acid. A. H.

α-Diketones. By PAVEL IW. PETRENKO-KRITSCHENKO and E. ELTSCHANINOFF (*Ber.*, 1901, **34**, 1699—1702).—α-Diketones resemble aldehydes, and are distinguished from monoketones by the ability they possess of forming hydrazones with phenylhydrazine hydrochloride. Thus dimethyl diketone reacts immediately at the ordinary temperature with phenylhydrazine hydrochloride, forming a *monophenylhydrazone* melting at 135°, and on heating at 100°, a *diphenylhydrazone* melting at 239°. Methyl ethyl diketone behaves similarly. The reaction between phenylhydrazine and various ketones has been quantitatively studied. Mol. proportions of the ketone and phenylhydrazine in alcoholic solution are mixed and kept for 1 hour at a temperature of 15—17°; the remaining phenylhydrazine is then estimated. With acetone, 74·0 per cent. of the phenylhydrazine had combined, with methyl ethyl diketone, 82·9 per cent., and with acetonylacetone, 30·6 per cent. Similarly, the aromatic α-diketone, benzil, was more reactive than the monoketone, phenyl benzyl ketone. Similar measurements made with cyclic α-diketones show that the ring formation serves still further to intensify the reactivity of the carbonyl groups. Thus under the above-mentioned conditions, benzil combined with 18 per cent. of the phenylhydrazine, acenaphthaquinone with 46·3, phenanthraquinone with 36·8, and retenequinone with 31·3 per cent. Sodium hydrogen sulphite also combines with these cyclic α-diketones, but not with benzil. K. J. P. O.

Acetochloro-dextrose, -galactose, and -lactose. By ZDENKO H. SKRAUP and R. KREMANN (*Monatsh.*, 1901, **22**, 375—384).—γ-Pentacetyldextrose (m. p. 112°) is easily prepared by allowing a mixture of dextrose and excess of acetyl chloride to remain for 8 days at the ordinary temperature (compare Königs and Erwig, Abstr., 1889, 952).

α-Pentacetyldextrose (m. p. 131°) when treated with phosphorus pentachloride and aluminium chloride by the method of von Arlt (this vol., i, 369), either at a low temperature or at 100°, yields an acetylchlorodextrose (hydrose), identical in all respects with the substance obtained from the γ-pentacetate. Acetochlorodextrose is most readily converted into the α-pentacetyldextrose by the action of dry, finely-powdered silver acetate on its solution in acetic acid. Boiling with acetic acid brings about the same change, but more slowly.

Acetylchlorogalactose, $C_{14}H_{19}O_9Cl$, is obtained by the action of phosphorus pentachloride and aluminium chloride on pentacetylgalactose, and forms white needles melting at 82° (compare Fischer and Armstrong, this vol., i, 189), very soluble in ether, chloroform, alcohol, or benzene. Treated with silver acetate in acetic acid solution, pentacetylgalactose (m. p. 142°) is reformed.

Phenylhydrazine acts readily on both the above acetylchloro-derivatives; phenylhydrazine hydrochloride, and acetylphenylhydrazine were alone isolated. K. J. P. O.

Galactosamine. By Friedrich N. Schulz and Fritz Ditthorn (*Zeit. physiol. Chem.*, 1901, **32**, 428—434).—Galactosamine has been prepared from galactosazone by Fischer's method (Abstr., 1886, 933). Its oxalate was obtained in a crystalline state, but was always mixed with a certain amount of ammonium oxalate. In its properties, it appears to be identical with the galactosamine previously obtained from the glucoproteid of the albuminous gland of the frog (Abstr., 1900, i, 478). J. J. S.

Refraction of Aqueous Carbohydrate Solutions. II. Muta-rotating Sugars (Disaccharides) and Non-muta-rotating Sugars. By F. Stolle (*Zeit. Ver. deut. Zuckerind.*, 1901, 469—487. Compare this vol., i, 368).—For aqueous lactose solutions, the following results have been obtained:

	Ten minutes after solution.			Twenty-four hours after solution.		
Number of solution.	Concentration (grams per 100 c.c.).	Sp. gr. at 17·5°/4°.	n_D.	Concentration (grams per 100 c.c.).	Sp. gr. at 17·5°/4°.	n_D.
1	1·0027	1·00204	1·33473	1·0028	1·00218	1·33473
2	2·0073	1·00617	1·33597	2·0074	1·00626	1·33588
3	4·0025	1·01357	1·33882	4·0027	1·01361	1·33873
4	8·0146	1·02842	1·34465	8·0167	1·02869	1·34448

Thus, with lactose solutions, the alteration in the refractive index is not in the same sense as with the hexoses, an increase in the sp. gr. being accompanied by a decrease in the refractive index. Solutions of the hexoses, with the exception of dextrose, show no variability of the specific refraction (Lorentz and Lorenz formula) with time or concentration, but the values for lactose show a diminution corresponding with the diminution of the refractive index.

The refractive indices of aqueous solutions of sucrose and raffinose have also been determined, the results being given in tables.

Tables are also given showing for solutions of dextrose, lævulose, galactose, sucrose, lactose, and raffinose the values of n_D at 17·5°

corresponding with any concentration of the sugar solution. Where a pure solution of any sugar is available, the measurement of its refractive index serves as a convenient means of determining its concentration; this method is of especial value where only small quantities of liquid can be obtained, a few drops being sufficient for use with Abbe's small direct vision refractometer, whilst with the Pulfrich instrument, which allows of more accurate measurements, about 5 c.c. are required. T. H. P.

Nitrocelluloses. By GEORG LUNGE and J. BEBIE (*Zeit. angew. Chem.*, 1901, **14**, 483—488, 507—515, 537—543 and 561—568. Compare Lunge and Weintraub, Abstr., 1899, i, 559).—The addition of water to the nitrating mixture of sulphuric and nitric acids lessens the percentage of nitrogen contained in the product. With a mixture containing 16·61 to 20·26 per cent. of water, the products obtained at the ordinary temperature are completely soluble in an ether-alcohol mixture, but with a further increase in the percentage of water, the solubility of the product decreases. The authors are not able to confirm Wyss-Naef's statements (*Zeit. angew. Chem.*, 1899, **12**, 469). When considerable amounts of water are present and the reaction is continued for some time, the products have the properties of oxy- or perhaps oxynitro-celluloses. When higher temperatures are employed, namely, 40—60°, it is not advisable to prolong the operation, as secondary reactions occur which lower the percentage of nitro-products; the nitration is complete at the end of 15 minutes at 60° with a mixture containing about 19 per cent. of water, and the product is completely soluble. The percentage of water also affects the structure of the product. Mixtures containing less than 15 per cent. of water do not destroy the structure of the cellulose; with mixtures containing 18 per cent. the threads appear to be drawn together, and with still higher percentages the structure becomes completely destroyed, the maximum being obtained with mixtures containing 23—25 per cent. of water.

Increasing the ratio of nitric to sulphuric acid from 1 : 1 to 1 : 3 raises the percentage of nitrogen; further increase to 1 : 4 or 1 : 5 has but little influence on the percentage of nitrogen.

The formation of oxynitrocelluloses by the action of dilute nitric acid (sp. gr. 1·4) is greatly increased by the addition of sulphuric acid; an addition of 5 per cent. doubles the formation of the oxy-compounds. It appears that a nitrocellulose containing 12·8 per cent. of nitrogen exists in both a soluble and an insoluble modification.

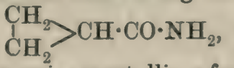
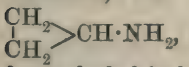
Products containing 13·83 per cent. of nitrogen, and probably corresponding with a dodecanitrate, can be obtained by using a mixture of sulphuric acid 62·95, nitric acid 24·95, and water 12·10 per cent. The product is, however, unstable, and when kept for some months, the percentage of nitrogen sinks to 13·5. With mixtures of sulphuric and fuming nitric acids, the highest nitration product appears to be a nondecanitrocellulose, which can more readily be obtained by a mixture of acids containing 10—12 per cent. of water. With a temperature of 32°, the maximum nitration is reached after 1 hour; an increase in the time favours denitration.

Nitrocelluloses containing 11 to 11·6 per cent. of nitrogen are soluble in ether-alcohol (3 : 1), also to a certain extent in absolute alcohol, but are insoluble in absolute ether or 95 per cent. alcohol. They are also readily soluble in ether-alcohol 6 : 1, but not so readily in mixtures 9 : 1 or 12 : 1, or in mixtures 1/6 : 1 or 1/12 : 1.

The presence of nitric peroxide in the nitrating mixture does not appear to affect the yield of nitro-products, or yet the stability of the same. Mixtures containing 8—11 per cent. of water yield products which are just as stable as those obtained with mixtures of pure acids.

Celluloses from different sources appear to yield identical products when nitrated in the same way (compare Nettlefold, Abstr., 1887, 792).

Morton-Liebschütz's method of differentiating between hexa- and penta-nitrocelluloses by the aid of polarised light (*Mon. Sci.*, 1891, 119) is worthless, as the same fibre can give both blue and grey colours under slightly different conditions. The method, however, can be used to distinguish between unaltered cellulose which iridesces, and highly nitrated products which give a blue shimmer if the structure of the fibre is still retained. J. J. S.

An Amine from Trimethylenecarboxylic Acid. By NIC. M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 377—383).—Ethyl trimethylenecarboxylate, already prepared by Perkin (Trans, 1885, **47**, 815), has the sp. gr. 0·9681 at 15°/4°, and n_D 1·4217 at 15°; the molecular refraction is hence 29·90, the calculated value being 29·47. The *amide* of trimethylenecarboxylic acid,  $\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>CH\cdot CO\cdot NH_2$, prepared from the ethyl ester by the action of ammonia, crystallises from water or alcohol in stout, rectangular plates, and from benzene in long needles, melting at 124—125°. By the action of potassium hypobromite, the amide is converted into an *amine* of the composition $C_3H_5\cdot NH_2$, which boils at 49°, and has a strong ammoniacal odour recalling that of propylamine; it mixes in all proportions with water, and absorbs carbon dioxide from the air, forming a solid carbonate. It has a sp. gr. 0·8254 at 20°/20° and 0·8240 at 20°/4°, and n_D is 1·421 at 20°; the value of the molecular refraction is 17·17, the calculated number being 17·32. The constitution of the amine is as yet unsettled, but it may be represented either by the formula  $\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>CH\cdot NH_2$, or by $CH_2{:}CMe\cdot NH_2$. The *hydrochloride* separates from alcohol in large, colourless plates melting at 100—101°. By the action of phenylthiocarbimide on a benzene solution of the amine, *phenyltrimethylenylthiocarbamide*, $NHPh\cdot CS\cdot NH\cdot C_3H_5$, is obtained; it crystallises from alcohol in hexagonal plates melting at 123—123·5°.

T. H. P.

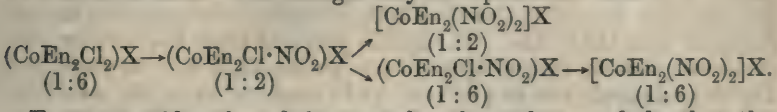
Action of Nitrous Acid on Tetramethylenylmethylamine [ω-Aminomethyl*cyclo*butane]; Methylenotetramethylene Bromide. By NICOLAUS I. DEMJANOFF and M. LUSCHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 279—283).—The action of nitrous acid on an aqueous solution of ω-aminomethyl*cyclo*butane hydrochloride yields (1) the alcohol obtained by Perkin (Trans., 1901, **79**, 329) by reducing the chloro-anhydride of tetramethylenecarboxylic acid; (2) a hydrocarbon which energetically combines with bromine, giving a *bromide* of the composition $C_5H_8Br_2$; the latter is a colourless liquid boiling at 191—192° under 750 mm. pressure, and having an odour recalling, but less sharp than, that of ethylene bromide. T. H. P.

Stereoisomeric Cobalt Compounds. By ALFRED WERNER (*Ber.*, 1901, **34**, 1705—1719).—Dichlorodiethylenediaminecobalt salts, $(CoEn_2Cl_2)X$ (where "En" = ethylenediamine) exist in two isomeric forms, distinguished chiefly by physical properties. The "praseo"-salts are green, and the "violeo"-salts are violet, and correspond respectively to the "flavo"- and "croceo"-dinitrotetrammine salts, $[Co(NO_2)_2(NH_3)_4]X$. The author believes that the two series are stereoisomeric, and represents them by the space formulæ previously described (Abstr., 1893, ii, 379). The notation based on this formula represents the "praseo" as 1 : 6-salts and the "violeo" as 1 : 2. Similarly, two series of dinitritodiethylenediamine-, $[CoEn_2(NO_2)_2]X$, and chloronitritodiethylenediamine-cobalt salts, $(CoEn_2Cl\cdot NO_2)X$, exist. Both series of salts possess a mol. conductivity which shows that they form in solution two ions; they do not give the reactions of nitrites, and with silver hydroxide their chlorides give strongly alkaline solutions of the base. In the 1 : 6-series, hydrated or acid salts are frequently formed, whilst in the 1 : 2-series such salts are not formed. The 1 : 2-dinitrito-salts are more sparingly soluble, and have a deeper colour than the 1 : 6-salts. The 1 : 2-chloronitrito-salts are reddish-orange in colour, whilst the 1 : 6-salts are yellowish-orange.

The nitrites of both series of dinitrito-salts are obtained by the action of ethylenediamine on potassium cobalt hexanitrite. By the action of sodium nitrite on 1 : 6-dichlorodiethylenediaminecobalt salts, 60 per cent. of the 1 : 6- together with 40 per cent. of the 1 : 2-dinitrito-salts is formed. The 1 : 2-dichloro-salts under the same conditions yield only the 1 : 2-dinitrito-salt. The 1 : 6-salts can also be obtained free from 1 : 2-salts by oxidation by atmospheric oxygen of a solution of cobaltous chloride containing ethylenediamine and sodium nitrite. The 1 : 6-dinitritosulphate and iodide can be completely converted into the corresponding 1 : 2-salts by simply evaporating their aqueous solutions to dryness. The 1 : 6-nitrate and nitrite, on the other hand, cannot be thus transformed.

By the action of nitric acid on both the 1 : 2- and 1 : 6-dinitrito-salts, one of the NO_2 groups becomes displaced by a NO_3 group, and nitratonitrito-compounds, $[CoEn_2(NO_2)NO_3]X$, are obtained. This reaction contrasts with the action of hydrochloric acid on the dinitrito-salts; only the 1 : 6-salts yield a chloronitrito-salt, whilst the 1 : 2-salts give a dichloro-salt. The author thinks that as nitric acid behaves with each series in a similar manner, the reaction with hydrochloric acid is not sufficient evidence for the existence of two different constitutions in the two series of salts (compare Jörgensen, Abstr., 1899, ii, 293).

When the 1 : 6-dichlorodiethylenediaminecobalt chloride is treated with sodium nitrite, the nitrite $(CoEn_2Cl_2)NO_2$ first formed is rapidly transformed, in the absence of excess of nitrous acid, into the chloride of a chloronitrito-compound, $(CoEn_2Cl\cdot NO_2)Cl$, a transformation which is accompanied by a change of colour from green to brick-red. This chloronitrito-compound belongs to the 1 : 2-series, as with sodium nitrite it yields the 1 : 2-dinitrito-salts. On boiling a solution of the nitrate of this 1:2-chloronitrito-compound, it changes into the nitrate of the 1 : 6-chloronitrito-series, which with sodium nitrite yields the 1 : 6-dinitrito-salts. The changes may be represented thus :



$$\begin{tikzcd}[column sep=small] & & \underset{(1:2)}{[CoEn_2(NO_2)_2]X} & \\ \underset{(1:6)}{(CoEn_2Cl_2)X} \arrow[r] & \underset{(1:2)}{(CoEn_2Cl\cdot NO_2)X} \arrow[ur] \arrow[dr] & & \\ & & \underset{(1:6)}{(CoEn_2Cl\cdot NO_2)X} \arrow[r] & \underset{(1:6)}{[CoEn_2(NO_2)_2]X.} \end{tikzcd}$$

From a consideration of these results, the author concludes that the isomerism exhibited by dichloro-, chloronitrito-, and dinitrito-diethylenediaminecobalt salts is of the same order, and is not an isomerism due to difference of constitution, but to difference of spacial configuration, and most nearly allied to "cis-trans" isomerism. K. J. P. O.

Stereoisomeric Dinitritodiethylenediamine Cobalt Salts, $[CoEn_2(NO_2)]_2X$. By ALFRED WERNER and ED. HUMPHREY (*Ber.*, 1901, **34**, 1719—1732. Compare preceding abstract).—A mixture of the nitrites of the 1 : 2- and the 1 : 6-dinitritodiethylenediamine compounds is obtained when potassium cobalt hexanitrite, $Co(NO_2)_6K_3$, and ethylenediamine are warmed together in aqueous solution.

1 : 2-*Dinitritodiethylenediaminecobalt nitrite*, $[CoEn_2(NO_2)_2]NO_2$, forms 80 per cent. of the mixed salts, and separates first on fractional crystallisation. It crystallises in dark brown or black prisms and also in light brown needles. The *nitrate* is prepared by the action of nitric acid on the preceding salt, and crystallises in long, lustrous, four-sided prisms of a light brown colour which exhibit dichroism and are very insoluble in water. It explodes at 200°, and when evaporated with nitric acid, it yields a mixture of a nitritonitrato-, $[CoEn_2(NO_2)\cdot NO_3]NO_3$, and a dinitrato-diethylenediaminecobalt nitrate, $[CoEn_2(NO_3)_2]NO_3$. With solutions of various salts, this 1 : 2-nitrate gives a number of precipitates, which serve to distinguish it from the isomeric 1 : 6-salt. The *chloride* prepared from the nitrite by treating it with hydrochloric acid in the presence of carbamide, crystallises in broad, brown plates, which are converted into 1 : 6-dichlorodiethylenediaminecobalt chloride by hydrochloric acid. The *bromide* is prepared by neutralising with hydrobromic acid a solution of the base which is obtained by shaking up a cold solution of the chloride with moist silver hydroxide. This salt crystallises in dark brown plates resembling the chloride. The *iodide*, prepared in a similar manner, forms reddish-brown prisms; the *sulphate*, prepared from the nitrate and ammonium sulphate, crystallises in silky, light brown, very insoluble needles. Determinations of the electrical conductivity of the above salts gave values for μ varying from 90—100 at a dilution $v=1024$. The *platinichloride* is very insoluble, and crystallises in microscopic prisms terminated by pyramids; the *platinochloride* forms orange leaves, the *aurichloride*, golden-brown needles.

1:6-*Dinitritodiethylenediaminecobalt nitrite*, $[CoEn_2(NO_2)_2]NO_2,2H_2O$, is separated from its isomeride by fractional crystallisation, and crystallises in brownish-yellow rhombs which very readily effloresce. The *nitrate* forms large plates which are very insoluble; with nitric acid, it yields red nitritonitrato-salts. The *chloride*, with $2H_2O$, prepared from the base and hydrochloric acid, or from the iodide and silver chloride, crystallises in pale yellow, four-sided prisms, which effloresce, and are converted by hydrochloric acid into chloronitrito-salts. For the foregoing salts, μ has the value 90—100 for $v = 1024$. The *bromide* crystallises with $2H_2O$ in light brown prisms, and is prepared from the iodide. The *iodide*, prepared from the nitrate and potassium iodide, forms light brown plates, little soluble in water. The *sulphate* could not be prepared, as in evaporation of its solutions it transformed into the isomeric 1 : 2-salt. The *platinichloride* crystallises in pale yellow needles, and the *platinochloride* in brown plates.

K. J. P. O.

1:6-Chloronitritodiethylenediaminecobalt Salts, $(CoEn_2Cl{\cdot}NO_2)X$. By Alfred Werner (*Ber.*, 1901, **34**, 1733—1738).—A pure neutral solution of 1 : 6-dichlorodiethylenediaminecobalt chloride (prepared by Jörgensen's method, Abstr., 1889, 351) is stirred with a rod of sodium nitrite. The colour changes from green to red, and bright red crystals of the 1 : 2-chloronitrito-chloride separate; the latter is converted into the nitrate by the action of nitric acid.

1 : 6-*Chloronitritodiethylenediaminecobalt nitrate*, prepared by boiling an aqueous solution of the 1 : 2-chloronitrito-nitrate, crystallises in red, four-sided crystals. With nitric acid, it forms an *acid* salt, a red, lustrous, crystalline powder which is decomposed by water into nitric acid, and the normal salt, the same change occurring when it is kept in a desiccator. The *iodide*, prepared from the nitrate and potassium iodide, forms brownish-orange plates; the *chloride*, which crystallises with $1H_2O$, forms red plates; the *thiocyanate* crystallises in sparingly soluble needles.

K. J. P. O.

1 : 2-Chloronitritodiethylenediaminecobalt Compounds. By Alfred Werner and L. Gerb (*Ber.*, 1901, **34**, 1739—1745. Compare previous abstract).—1 : 2-*Chloronitritodiethylenediaminecobalt chloride*, $(CoEn_2Cl{\cdot}NO_2)Cl$, prepared as previously described (*loc. cit.*) from 1 : 6-dichlorodiethylenediamine nitrite, crystallises in light red, lustrous needles, which are converted by concentrated hydrochloric acid into 1 : 6-dichlorodiethylenediaminecobalt chloride. The *nitrate*, prepared from the chloride, forms red leaves sparingly soluble in water, and decomposed in aqueous solution into the 1 : 6-isomeride. The *acid sulphate*, prepared from the chloride and concentrated sulphuric acid, forms a dark red, amorphous powder insoluble in cold water and decomposed by hot water. The *nitrite* crystallises in microscopic prisms, which are converted in aqueous solution into the dinitritodiethylenediaminecobalt chloride. The *iodide* forms a red, crystalline precipitate; the *bromide* resembles the iodide; both are changed by heating with water. The *thiocyanate* crystallises in brick-red prisms which readily transform into the thiocyanonitrito-salt, $[CoEn_2(NO_2){\cdot}SCN]Cl$.

By the action of silver nitrate on the chloride just described, the *nitrate* of a nitratonitrito-compound, $[CoEn(NO_2){\cdot}NO_3]NO_3$, is obtained as a pale yellow, crystalline precipitate. The nitrate of the 1 : 2-

chloronitrito-compound, both with sodium and silver nitrite, yields a 1 : 2-dinitrito-salt. K. J. P. O.

Alcohol Bases. By HERMANN MATTHES (*Annalen*, 1901, **316**, 311—317. Compare this vol., i, 259).—*Ethanoldipropylamine* (*hydroxyethyldipropylamine*), $NPr_2 \cdot CH_2 \cdot CH_2 \cdot OH$, is a colourless oil boiling at 195—196° under 758 mm. pressure, obtained by mixing dipropylamine with ethylene oxide in the presence of water; it volatilises in steam and is strongly basic, having an ammoniacal odour; it has a sp. gr. 0·8576 at 20°/0°, n_D 1·4402 at 20°, and molecular refraction 44·566, the theoretical value for this constant being 44·494. The *picrolonate*, $C_8H_{19}NO,C_{10}H_8O_5N_4$, and *picrate* melt respectively at 128—130° and 80—82°.

*Ethanoldi*iso*butylamine* (*hydroxyethyldi*iso*butylamine*),

$$N(C_4H_9)_2 \cdot CH_2 \cdot CH_2 \cdot OH,$$

obtained in a similar manner to the preceding base, is a colourless oil boiling at 213—214° under 754 mm. pressure; it has a sp. gr. 0·8407 at 20°/4° and n_D 1·4355 at 20°, the molecular refraction calculated from the refractive index being 53·753, whilst the theoretical value is 53·70. The *picrolonate* and *picrate* are yellow, crystalline salts melting respectively at 134—135° and 123—125°; the *aurichloride* is somewhat insoluble in cold water or alcohol, it separates at first as an oil, and then solidifies in the cold to yellow, rhombic crystals melting at 86—88°.

*Ethanoldi*iso*amylamine* (*hydroxyethyldi*iso*amylamine*),

$$N(C_5H_{11})_2 \cdot CH_2 \cdot CH_2 \cdot OH,$$

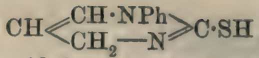
prepared by heating its generators in sealed tubes at 150°, is a colourless oil having an odour resembling that of amyl alcohol; it boils at 247—248° under 748 mm. pressure, and has a sp. gr. 0·8492 at 20°/4° and n_D 1·4435 at 20°, the experimentally determined and calculated values of the molecular rotation being 62·815 and 62·906. The *picrolonate* crystallises in hexagonal leaflets melting at 88°; the picrate is oily. These bases are sparingly soluble in water, the solubility diminishing as the homologous series is ascended; their aqueous solutions have a strongly alkaline reaction; they readily dissolve in the ordinary organic solvents. G. T. M.

Aminoacetals and Aminoaldehydes. By ALFRED WOHL (*Ber.*, 1901, **34**, 1914—1924).—[With M. WOHLBERG.]—When β-chloropropaldehyde diethylacetal is treated with alcoholic ammonia, a mixture of *β-aminopropaldehyde diethylacetal*,

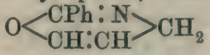
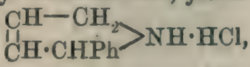
$$NH_2 \cdot CH_2 \cdot CH_2 \cdot CH(OEt)_2,$$

and the secondary *base*, $NH[C_2H_4 \cdot CH(OEt)_2]_2$, is obtained; the former is a colourless, basic liquid having a sp. gr. 0·9359 at 17°, boils at 80° (corr.) under 18 mm. pressure, and when treated with oxalic acid yields the crystalline *oxalate* of β-aminopropaldehyde,

$$NH_2 \cdot [CH_2]_2 \cdot CHO,H_2C_2O_4,H_2O,$$

which, when anhydrous, melts at 98°. The *platinichloride* of the aminoaldehyde is soluble in water and insoluble in alcohol. Phenylthiocarbimide combines with the acetal and yields the *thiocarbamide*, $NHPh \cdot CS \cdot NH \cdot C_2H_4 \cdot CH(OEt)_2$, which forms colourless crystals, melts at 85° (corr.), and when treated with concentrated hydrochloric acid yields *phenyldihydropyrimidyl mercaptan*,  $\mathrm{CH}<\begin{matrix}\mathrm{CH\cdot NPh}\\ \mathrm{CH_2—N}\end{matrix}>\mathrm{C\cdot SH}$; this crystallises from water, melts at 151°, is acid in character, but forms a crystalline *platinichloride.* The *carbamide*,

$$\mathrm{NH_2\cdot CO\cdot NH\cdot C_2H_4\cdot CH(OEt)_2},$$

obtained by treating a neutralised solution of the aminoacetal with potassium cyanate, forms deliquescent crystals melting at 61°. The *benzoyl* derivative of the aminoacetal is a pale yellow syrup and, when treated with oxalic acid, forms *phenyl*-1 : 3-*oxazine*,  $\mathrm{O}<\begin{matrix}\mathrm{CPh:N}\\ \mathrm{CH:CH}\end{matrix}>\mathrm{CH_2}$ which crystallises from alcohol and melts at 171°; the *acetyl* derivative is a yellow oil of sp. gr. 0·9937 at 17°; the *benzylidene* derivative, obtained by the condensation of the aminoacetal with benzaldehyde, is a colourless oil of sp. gr. 0·9878 at 17°, boils at 157° under 11 mm. pressure and, when reduced, yields the *benzyl* derivative, which is a yellowish oil of sp. gr. 0·9799 at 17°, boils at 156° under 14 mm. pressure and, when treated with concentrated hydrochloric acid, yields the *hydrochloride* of phenyldihydropyrrole,  $\begin{matrix}\mathrm{CH—CH_2}\\ \|\\ \mathrm{CH\cdot CHPh}\end{matrix}>\mathrm{NH\cdot HCl}$, which melts at 240° (corr.).

[With K. SCHÄFER.]—*β-Cyanopropaldehyde diethylacetal*, obtained by the action of potassium cyanide on the corresponding chloro-compound, is an oil boiling at 106° under 45 mm. pressure and when reduced by sodium in alcoholic solution yields *γ-aminobutyraldehyde diethylacetal*, which is a colourless basic oil boiling at 196° or at 96° under 21 mm. pressure. R. H. P.

Action of Alkyl Thiocyanates and Alkyl *iso*Thiocyanates [Thiocarbimides] with Thiol Acids. By HENRY L. WHEELER and HENRY F. MERRIAM (*J. Amer. Chem. Soc.*, 1901, **23**, 283—299).—By the action of thioacetic acid on ethyl thiocyanate, Chanlaroff (Abstr., 1883, 39) obtained ethyl acetyldithiocarbamate. The authors have confirmed this, and have found that acyldithiocarbamates may be readily prepared by warming a benzene solution of the thiocyanate for a few hours with thioacetic or thiobenzoic acid. The compounds thus obtained are yellow, well crystallised substances, readily soluble in hot alcohol, and sparingly in cold; they dissolve in aqueous alkali, and are reprecipitated by carbon dioxide. *Methyl acetyldithiocarbamate*, $\mathrm{NHAc\cdot CS\cdot SMe}$, crystallises in long, slender, bright yellow prisms, and melts at 119°. By the action of ethyl bromide and sodium ethoxide on the corresponding ethyl ester, *ethyl acetyliminodithiocarbonate*, $\mathrm{NAc:C(SEt)_2}$, is obtained as a colourless oil which boils at 142°. *Propyl acetyldithiocarbamate* crystallises in brilliant yellow plates or prisms, and melts at 78°. *Cetyl thiocyanate*, $\mathrm{C_{16}H_{32}\cdot SCN}$, obtained by the action of cetyl iodide on potassium thiocyanate, boils at 242—249° under 30 mm. and at 222—227° under 13 mm. pressure, and, on cooling, solidifies as a white wax which melts at 15—15·5°. *Cetyl acetyldithiocarbamate* crystallises in slender needles, and melts at 89—90°; it dissolves in dilute alkali with formation of the *sodium* salt, which separates in thin, colourless plates. *Benzyl acetyldithiocarbamate* crystallises in bright yellow plates and melts at 136°.

Methyl benzoyldithiocarbamate forms slender yellow needles and melts at 135°. The corresponding *ethyl* ester crystallises in stout, yellow prisms and melts at 84°. *Methyl benzoyliminodithiocarbonate*, $NBz\dot{:}C(SMe)_2$, crystallises in long, colourless prisms, and melts at 46°, whilst the *ethyl* ester is obtained as an oil which boils at 220—221° under 17 mm. pressure. When the methyl ester is dissolved in excess of alcoholic ammonia and left for 2 days, mercaptan separates, and *benzoyl-ψ-methylthiocarbamide*, $NBz\dot{:}C(SMe)\cdot NH_2$, is produced, melting at 111—112°. *Benzoyl-ψ-methylphenylthiocarbamide*, $NBz\dot{:}C(SMe)\cdot NHPh$, obtained by warming the methyl benzoyliminodithiocarbonate with aniline, forms thin, colourless plates and melts at 104—105°. *Benzoyl-ψ-ethylphenylthiocarbamide* crystallises in long, colourless prisms and melts at 87—88°. *Propyl benzoyldithiocarbamate* crystallises in bright yellow prisms and melts at 77°. The iso*butyl* ester forms golden yellow needles and melts at 80—81°. The *cetyl* ester crystallises in bright yellow plates and melts at 63—64°. Benzyl thiocyanate melts at 43—43·5°. *Benzyl benzoyldithiocarbamate* crystallises in long, yellow needles, melts at 108°, and yields a *sodium* salt which separates in thin, colourless plates.

If phenyl thiocyanate is heated with thiobenzoic acid, phenyl thiolbenzoate is produced. Phenyl thiocyanate is not readily converted into phenylthiocarbimide; if left for 4 weeks at 34—36°, it remains practically unaltered. When 2:4-dinitrophenyl thiocyanate is heated with thioacetic acid, tetranitrophenyl disulphide is obtained, whilst by the action of thiobenzoic acid, benzoyldinitrophenyl mercaptan is produced, which is converted by alkalis into tetranitrophenyl disulphide. Thiocyanoacetylethylurethane reacts with thiobenzoic acid with formation of *benzoyldithiocarbamicacetylethylurethane*,

$$NHBz\cdot CS\cdot S\cdot CH_2\cdot CO\cdot NH\cdot CO_2Et,$$

which crystallises in thin, golden-yellow plates and melts at 159°. By the action of thiobenzoic acid on methyl thiocyanoacetate, *methyl benzoyldithiocarbamicacetate*, $NHBz\cdot CS\cdot S\cdot CH_2\cdot CO_2Me$, is obtained, which crystallises in bright yellow prisms and melts at 118°. When thiocyanoacetamide is heated with thiobenzoic acid, hydrogen cyanide, benzoyl disulphide, and a black, tarry substance are produced. *Benzoylthioglycollamide*, $SBz\cdot CH_2\cdot CO\cdot NH_2$, obtained from potassium thiolbenzoate and chloroacetamide, crystallises from hot water in long, colourless prisms and melts at 119—120°. When thiocyanomethylacetanilide is heated with thiobenzoic acid, *benzoyldithiocarbamicmethylacetanilide*, $NHBz\cdot CS\cdot S\cdot CH_2\cdot CO\cdot NMePh$, is obtained in yellow prisms melting at 152°.

Allylthiocarbimide and thiobenzoic acid react with formation of carbon disulphide and allylbenzamide, and by the action of thiobenzoic acid on phenylthiocarbimide, carbon disulphide and benzanilide are produced; similarly, thioacetic acid reacts with phenylthiocarbimide to form acetanilide. 2-*Chloroallylbenzamide*, $NHBz\cdot CH_2\cdot CCl\dot{:}CH_2$, obtained by the action of thiobenzoic acid on α-chloroallylthiocarbimide, crystallises in long, colourless prisms and melts at 95°. Benzoylthiocarbimide reacts with thiobenzoic acid with formation of dibenzamide.

Ethyl selenocyanate, EtSeCN, obtained by the action of ethyl bromide on potassium selenocyanate, is a pale yellow oil of unpleasant odour, which boils at 172° under 741 mm. pressure; it reacts with thiobenzoic acid, but the products have not been investigated.

E. G.

Thiocyanogen, the so-called ψ-Thiocyanogen and the Yellow Colouring Matters obtained from Thiocyanates. By Alwin Goldberg (*J. pr. Chem.*, 1901, [ii], **63**, 465—495).—After considering the previous work on the subject, of which a summary is given, the author comes to the conclusion that thiocyanogen, $(CNS)_x$, has not been obtained in a pure state.

The author finds that the ψ-thiocyanogen, obtained by oxidising thiocyanates by potassium chlorate and hydrochloric acid, becomes changed into the dye "canarin," when treated with alkalis. This dye, prepared from its sodium salt, has the formula $C_8H_6ON_8S_7$, and represents about half the ψ-thiocyanogen from which it is formed.

The same ψ-thiocyanogen and dye are obtained by the action of excess of chlorine on thiocyanates. The investigation of the action of bromine on potassium thiocyanate shows that the best yield of ψ-thiocyanogen is obtained when molecular quantities of thiocyanate and bromine are employed. At the same time, oxidation to sulphate and cyanic acid always takes place to a considerable extent. Perthiocyanic acid is also formed in the reaction. Nitric acid in various proportions converts about 27 per cent. of potassium thiocyanate into ψ-thiocyanogen; considerable oxidation to sulphuric acid, etc., occurs, and a little perthiocyanic acid is formed.

K. J. P. O.

A peculiar Double Cyanide. By Otto Herting (*Zeit. angew. Chem.*, 1901, **14**, 585—586).—See this vol., ii, 534.

Preparation of Fulminates. By Francesco Angelico (*Atti Real. Accad. Lincei*, 1901, [v], **10**, i, 476—478).—In place of the old method, which causes a copious evolution of an explosive mixture consisting mainly of ethyl nitrite and nitrate, the author gives the following for the preparation of mercury fulminate. A concentrated aqueous solution of malonic acid is added to a solution of mercury in excess of dilute nitric acid. The reaction generally begins spontaneously if the liquid be hot, but if not, the addition of a few drops of sodium nitrite solution causes an evolution of carbon dioxide, which gradually increases until it becomes tumultuous. Towards the end of the action, mercury fulminate separates as a white, crystalline powder which can be recrystallised from water. The first phase of the reaction is probably the formation of *iso*nitrosomalonic acid, which passes successively into *iso*nitromalonic acid, *iso*nitroacetic acid, and *iso*nitromethane, which then loses water, giving the oxime of carbonic oxide which Nef regards as fulminic acid. When cyanoacetic acid is used in place of the malonic acid, an insoluble double mercury salt, the constitution of which is not yet decided, is obtained.

T. H. P.

Nitroso*iso*butyronitrile and its Derivatives. By Oscar Piloty and B. Graf Schwerin (*Ber.*, 1901, **34**, 1863—1870. Compare Abstr., 1898, i, 616).—Nitroso*iso*butyronitrile is readily obtained by the oxidation of the corresponding hydroxylamino-compound with chlorine water at 0°. When kept, it gradually changes to a blue liquid which rapidly decomposes into nitro*iso*butyronitrile, a compound $C_{12}H_{18}ON_4$, and nitric oxide. When treated with concentrated hydrochloric acid at 0°, it is converted into nitroso*iso*butyramide, melting at 158°. The same product is more readily obtained by the oxidation of the hydroxylamino-amide. *Nitro*iso*butyramide*, $NO_2{\cdot}CMe_2{\cdot}CO{\cdot}NH_2$, is obtained when the nitro-nitrile is shaken with hydrochloric acid saturated at 0°; it forms glistening plates, melts at 117—118°, and is only moderately soluble in ether.

The *ethylimino-ether* of *hydroxylamino*iso*butyric acid*,

$$OH{\cdot}NH{\cdot}CMe_2{\cdot}C(NH){\cdot}OEt,$$

in the form of its *hydrochloride* (with 2HCl) is obtained by passing hydrogen chloride into an alcoholic solution of the hydroxylaminonitrile at 0°; it melts and decomposes at about 108° and is somewhat unstable. When oxidised with chlorine and water at 0°, it yields *ethyl nitroso*iso*butyrate* in the form of colourless crystals melting at 89° to a blue oil. The oil previously described by Gomberg (Abstr., 1898, i, 354) as the nitroso-ester is more probably the ester of hydroxylamino*iso*butyric acid.

*Hydroxylamino*iso*butyramidine hydrochloride*,

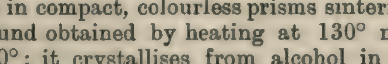
$$OH{\cdot}NH{\cdot}CMe_2{\cdot}C(NH){\cdot}NH_2,HCl,$$

melts and decomposes at 154°, dissolves readily in water, and on oxidation with chlorine water yields *nitroso*iso*butyramidine hydrochloride*, which melts and decomposes at 161°, is only sparingly soluble in cold water, and gives a precipitate with sulphuric acid. Other oxidising agents convert the hydroxylaminoamidine into different products. J. J. S.

Existence of Derivatives of Quadrivalent Nitrogen. I

By Oscar Piloty and B. Graf Schwerin (*Ber.*, 1901, **34**, 1870—1887).—Numerous experiments have been made in order to synthesise aliphatic azo-compounds by the condensation of amino-compounds with nitroso-derivatives, but so far without success. Nitroso*iso*butyronitrile and aniline in presence of acetic acid yield aminoazobenzene, which is undoubtedly formed by the elimination of nitrous acid from the nitroso-compound.

An aqueous solution of potassium cyanide reacts with nitroso*iso*butyramidine hydrochloride (compare preceding abstract) at 30° to 50°, yielding a basic compound, *porphyrexine*,

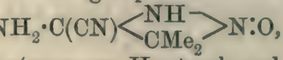


$$NH_2{\cdot}C(CN){<}\genfrac{}{}{0pt}{}{NH}{CMe_2}{>}N{\cdot}OH,3H_2O,$$

which crystallises in compact, colourless prisms sintering at 110°. The anhydrous compound obtained by heating at 130° melts and decomposes at 248—250°; it crystallises from alcohol in glistening, felted needles containing 1EtOH, but is practically insoluble in benzene or light petroleum, and the anhydrous compound is strongly hygroscopic. The *hydrochloride*, $C_5H_{10}ON_4,HCl$, crystallises in rhombic plates, melts and decomposes at 272°, and is readily soluble in water. The *oxalate* $(C_5H_{10}ON_4)_2,H_2C_2O_4,2H_2O$, forms prismatic needles melting and decomposing at 254°; the *sulphate* melts at 289°. When heated with hydrochloric acid at 100°, porphyrexine yields a compound,

$C_{10}H_{20}O_4N_6Cl_2$, probably the hydrochloride of the anhydride of an amino-acid. It crystallises in prisms, melts at about 192°, and is readily soluble in water or alcohol.

Hydrogen sulphide acts on porphyrexine suspended in alcohol yielding a *compound* $C_{10}H_{18}O_2N_6S_2$, probably a sulphur analogue of the anhydride formed by the action of hydrochloric acid. It crystallises from hot water in yellowish, rhombic prisms melting and decomposing at 231°, and is insoluble in most organic solvents with the exception of alcohol.

When reduced with sodium amalgam, porphyrexine is converted into a syrup, and when oxidised with potassium permanganate, or, still better, with potassium ferricyanide in the presence of alkali, it yields a basic compound, *porphyrexide*, $C_5H_9ON_4$, which crystallises in brick-red, prismatic plates melting and decomposing at 157°; this is only sparingly soluble in cold water, more readily in hot alcohol, but gradually undergoes decomposition. It has strong oxidising properties, reacting with hydrogen sulphide or sulphur dioxide, and regenerating porphyrexine; it also oxidises hydrochloric acid, or acidified potassium iodide. It forms salts with both acids and bases. The *nitrate*, $C_5H_9ON_4,HNO_3$, crystallises in lemon-yellow plates melting and decomposing at 127°. The *sodium* salt, $C_5H_8ON_4Na,H_2O$, forms deep violet coloured crystals melting and decomposing at about 100°, and readily soluble in both water and alcohol. It is thought probable that this oxidation product has the formula  $NH_2{\cdot}C(CN){<}{}^{NH-}_{CMe_2}{>}N{:}O$, and contains a quadrivalent nitrogen atom (compare Hantzsch and Semple, Abstr., 1896, ii, 95). J. J. S.

Iminodithiocarbonic Esters, $RN{:}C(SR')_2$. By **Marcel Delépine** (*Compt. rend.*, 1901, **132**, 1416—1418).—Diethyl- and di*iso*butylformocarbothialdines with methyl iodide yield respectively the compounds $NEt{:}C(SMe)_2$ and $C_4H_9{\cdot}N{:}C(SMe)_2$, whilst with ethyl iodide dimethylformocarbothialdine yields the compound $NMe{:}C(SEt)_2$. The substituted iminodithiocarbonic esters are also readily obtained by the successive action of carbon disulphide and an alkyl iodide on a primary amine of the methane series. When oxidised with nitric acid, they yield a sulphonic acid and an amine, the central carbon atom being eliminated; when reduced by sodium in presence of alcohol, they yield a diamine and a sodium mercaptide. They also react with salts of mercury, silver, or platinum. C. H. B.

Action of Zinc Ethyl on Anhydrides of Organic Acids, Oxides, and Lactones. By **Emerich Granichstädten** and **Friedrich Werner** (*Monatsh.*, 1901, **32**, 315—334).—It is shown that acetic anhydride and zinc ethyl first form an additive product, $CH_3{\cdot}CEt(OZnEt){\cdot}OAc$, which then reacts with water, thus:

$$CH_3{\cdot}CEt(OZnEt){\cdot}OAc + 2H_2O = Zn(OH)_2 + C_2H_6 + C_2H_4O_2 + COMeEt.$$

Estimation of the ethane, acetic acid, and methyl ethyl ketone formed proved the correctness of this equation (compare Saytzeff, *Zeit. f. Chem.*, 1870, 107).

Butyric anhydride and zinc ethyl yield an analogous additive product, which when decomposed by water gives ethane, ethyl propyl ketone, and butyric acid. Zinc ethyl has no action on the oxides, ethylene oxide, the oxides from *iso*butylene glycol (Franke, Abstr., 1896, i, 404), diphenylene oxide, paraldehyde, &c.

With valerolactone, zinc ethyl reacts at a temperature of 80°, ethane is evolved, and from the solid residue, by the action of dilute sulphuric acid, an oil was obtained which proved to be dimethyloxetone (Fittig and Rasch, Abstr., 1890, 867 and 868). It is shown that the zinc ethyl has effected the condensation of two molecules of valerolactone, with elimination of water; the divalolactone thus formed is converted by water and zinc hydroxide or by sodium hydroxide into divalonic acid, which by boiling with dilute sulphuric acid yields dimethyloxetone (compare Fittig, *loc. cit.*).

Butyrolactone and zinc ethyl react when heated, with evolution of ethane; from the solid residue, by boiling with sulphuric acid until the evolution of carbon dioxide ceased, oxetone was obtained.

Phthalide and zinc ethyl do not react, even when heated at 170° for days. K. J. P. O.

o-*iso*Propyltoluene [*o*-Methyl*iso*propylbenzene]. By H. Sprinkmeyer (*Ber.*, 1901, **34**, 1950—1954).—*o-Methyl*iso*propylbenzene*, obtained by the action of sodium on a mixture of *o*-bromocumene and methyl iodide, is a colourless liquid boiling at 157°, has a sp. gr. 0·8582 at 18°/18° and n_D 1·495; when oxidised with potassium permanganate, it yields dimethylphthalide. When treated with fuming sulphuric acid at 50°, at least two *monosulphonic acids* are formed; one of these forms sparingly soluble salts, of which the *barium* (with H_2O), the *lead* (with $2H_2O$), the *copper* (with $8H_2O$), and the *potassium* (with $2H_2O$) salts are described, and a *sulphonamide*, which crystallises in clusters of needles and melts at 90°; the other acid forms more soluble salts and a *sulphonamide*, which crystallises in lustrous leaflets and melts at 105°. R. H. P.

Constitution of a Bromo-derivative of *iso*Butylbenzene. By F. Bodroux (*Bull. Soc. Chim.*, 1901, [iii], **25**, 628—629).—The substance, $C_{10}H_5Br_9$, obtained by the action of an excess of bromine, on a mixture of *iso*butylbenzene and aluminium bromide has probably the constitution represented by the formula $C_6Br_5{\cdot}CHBr{\cdot}CMeBr{\cdot}CHBr_2$.

T. M. L.

Alkylated Aminobenzenesulphonic Acids and *m*-Aminophenols. By Robert Gnehm and Th. Scheutz (*J. pr. Chem.*, 1901, [ii], **63**, 405—427).—The alkylation of *m*-aminobenzenesulphonic acid or of the salts of *m*-acetylaminobenzenesulphonic acid was not found possible. *Barium* m-*acetylaminobenzenesulphonate*, prepared by acetylating barium *m*-aminobenzenesulphonate, crystallises, with $2H_2O$, in colourless needles; the *sodium* salt, with $2H_2O$, forms needles melting at 184—185°. The free acid could not be isolated from the salts.

m-*Methylaminobenzenesulphonic acid*, $NHMe{\cdot}C_6H_4{\cdot}SO_3H$, prepared by sulphonating methylaniline, crystallises in long needles decomposing at 285—290°. The *sodium* and *barium* salts are anhydrous crystalline powders. An isomeric *acid* is obtained in the sulphonation of methylaniline if the temperature is allowed to rise; above 150°, it is alone formed; it crystallises in large, anhydrous plates decomposing at 244°. The *sodium* salt crystallises, with $3H_2O$, in white plates; the *barium* salt forms crystals with H_2O.

m-*Ethylaminobenzenesulphonic acid*, prepared by sulphonating ethylaniline, crystallises in needles decomposing at 294°, and having the affinity constant $K = 0{\cdot}0159$. The *sodium* salt crystallises in white leaflets with $2H_2O$; the *barium* salt forms anhydrous crystals.

m-*Ethylaminoazobenzenesulphonic acid*, prepared by the action of benzenediazonium salts on the sulphonic acid, crystallises in microscopic, yellow needles melting at 165°. Another *ethylaminobenzenesulphonic acid* is also obtained in sulphonating ethylaniline, and crystallises in anhydrous plates decomposing at 258°, and having the affinity constant $K = 0{\cdot}0125$. A consideration of the affinity constants of this acid and of the three aminobenzenesulphonic acids leads to the conclusion that it and its methyl analogue are both para-derivatives, whilst the methylaminobenzenesulphonic acid obtained by Mundelius (*Ber.*, 1874, 7, 1350) is an ortho-derivative. The *sodium* salt, $NHEt{\cdot}C_6H_4{\cdot}SO_3Na,3H_2O$, crystallises in plates or prisms; the *barium* and *silver* salts each crystallise, with H_2O, in plates.

m-*Benzylmethylaminobenzenesulphonic acid*,

$$CH_2Ph{\cdot}NMe{\cdot}C_6H_4{\cdot}SO_3H,H_2O,$$

crystallises in needles; the *sodium* salt, obtained by heating benzyl chloride with sodium *m*-methylaminobenzenesulphonate in the presence of sodium hydroxide, crystallises in small leaflets or needles with $2H_2O$; the *barium* salt, with $3H_2O$, forms white scales.

Sodium benzylethylaminobenzenesulphonate, obtained in like manner to the analogous methyl derivative, is anhydrous; the *barium* salt crystallises in prisms with $3H_2O$.

m-*Methylaminophenol*, $NHMe{\cdot}C_6H_4{\cdot}OH$, obtained by the action of molten potassium hydroxide on the sulphonic acid, is a solid which boils at 170° under 12 mm. pressure. m-*Ethylaminophenol* forms a white, crystalline powder melting at 62° and boiling at 176° under 12 mm. pressure. m-*Benzylethylaminophenol* is a solid.

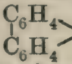
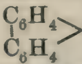
With phthalic anhydride, *m*-ethylaminophenol yields a phthalein, diethylrhodamine, which forms the main part of the Rhodamine 6 G. of commerce. The *phthalein* of *m*-benzylethylaminophenol is a reddish-brown powder the carmine-red solutions of which exhibit a yellow fluorescence.

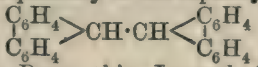
On nitrating benzylethylaniline at 0° in the presence of sulphuric acid, a *nitro*-derivative is obtained which forms red crystals. The nitro-group is in the para-position, as the base obtained on reduction does not give a rhodamine with phthalic anhydride, and gives a blue colour with ferric chloride. K. J. P. O.

Derivatives of 2-Chloronaphthalene. By KARL SCHEID (*Ber.*, 1901, **34**, 1813—1818).—By nitration in acetic acid solution, 2-chloronaphthalene is converted into 2 : 8-chloronitronaphthalene (Armstrong and Wynne, Proc., 1893, **9**, 166) which is accompanied by a number of higher nitro-products. When the 2-chloronaphthalene is directly treated with nitric acid or dissolved in sulphuric acid and then treated with nitric acid, during the addition of which it is cooled, the chief product is 2-*chloro*-1 : 6-*dinitronaphthalene*, which crystallises in short, yellow needles melting at 174°. The chlorine atom can very readily be replaced and the compound is converted by alcoholic ammonia into a *dinitronaphthylamine*, which crystallises in thin, dark yellow needles melting at about 218°. With acetic anhydride, it does not yield an acetyl derivative. This compound closely resembles the 1 : 6-dinitronaphthylamine of Gäss (Abstr., 1894, i, 605), but differs from it in melting point. When treated with nitrous acid, it yields nitronaphthalenediazoxide, which has also been obtained by Gäss. It follows from this that one of the nitro-groups is in position 1 ; the other is situated in the other ring, probably in position 6, since chlorodinitronaphthalene is converted by oxidation into a mononitrophthalic acid free from chlorine.

Aniline converts the chloro-compound into *phenyldinitronaphthylamine*, crystallising in slender, yellow needles, and α- and β-naphthylamine react in a similar manner.

2-*Chloro*-1 : 8-*dinitronaphthalene* can also be obtained by the nitration of β-chloronaphthalene under special conditions, and crystallises in thin, lustreless, yellow needles melting at 175°. With alcoholic ammonia, it yields 1 : 8-*dinitro*-2-*naphthylamine*, which crystallises in brown tablets melting at 222°, and can readily be converted, by means of the diazo-reaction, into 1 : 8-dinitronaphthalene. A *chlorotrinitronaphthalene* (probably 2-chloro-1 : 6 : 8-trinitronaphthalene) accompanies the dinitro-compounds and melts at about 145°. A. H.

A Potassium Derivative of Fluorene. By RUDOLF WEISSGERBER (*Ber.*, 1901, **34**, 1659—1661).—In accord with the recently observed acid nature of the methylene group of fluorene, the latter, when fused with potassium hydroxide at 280°, yields a *potassium* derivative,  $\left.\begin{array}{l}C_6H_4\\ C_6H_4\end{array}\right>CHK$, which forms a yellowish-brown, amorphous mass readily absorptive of water and carbon dioxide. The formation of this compound can be utilised to purify commercial fluorene, as it is readily decomposed by water, yielding the parent hydrocarbon. With compounds containing halogens, it readily combines ; thus with benzyl chloride it yields *phenyldiphenylene-ethane*,  $\left.\begin{array}{l}C_6H_4\\ C_6H_4\end{array}\right>CH\cdot CH_2Ph$, which crystallises from heavy petroleum in long, colourless prisms and melts at 149—150°. A small quantity of bis-diphenylene-ethane,

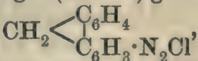


$$\left.\begin{array}{l}C_6H_4\\ C_6H_4\end{array}\right>CH\cdot CH\left<\begin{array}{l}C_6H_4\\ C_6H_4\end{array}\right.$$

(De la Harpe and van Dorp, this Journal, 1876, i, 242 ; Graebe, Abstr., 1893, i, 38) is also formed.

Indene fails to yield a potassium compound, although the corresponding derivative of *cyclo*pentadiene has recently been isolated (Thiele, this vol., i, 182). W. A. D.

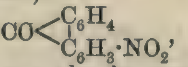
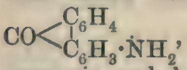
Fluorene. I. By OTTO DIELS (*Ber.*, 1901, **34**, 1758—1768).—2-Nitrofluorene (Strasburger, Abstr., 1884, 754) is best reduced to 2-aminofluorene by the action of zinc dust and calcium chloride on an aqueous alcoholic solution; 2-aminofluorene crystallises in needles and melts at 130° (corr.). Strasburger (*loc. cit.*) gives the m. p. as 124—125°.

2-*Diazofluorene chloride*,  $CH_2<\begin{array}{l}C_6H_4\\ |\\ C_6H_3\cdot N_2Cl\end{array}$, forms minute, yellow needles containing $2H_2O$, decomposes at 119—120° (corr.), dissolves in 40 parts of water at 18°, is more readily soluble in hot water, from which it crystallises on cooling, but is decomposed when boiled with water; the *bromide* forms white, felted needles, the *iodide* is yellow, the *mercurichloride* and *platinichloride* are yellowish, and the *dichromate* is orange-coloured.

2-*Hydroxyfluorene*, $C_{13}H_9\cdot OH$, prepared by boiling the diazochloride with water, sinters at 166° and melts at 171° (corr.), is slightly soluble in hot water, from which it crystallises in flakes, dissolves readily in dilute alkalis and in organic solvents, and gives no coloration with ferric chloride; the *potassium* salt is precipitated in minute needles on adding concentrated potassium hydroxide to its aqueous solution.

2-*Fluorylhydrazine*, $C_{13}H_9\cdot N_2H_3$, crystallises from hot alcohol in colourless flakes and from chloroform in four-sided, rhombic tablets, sinters at 165°, and melts at 170—171° (corr.), reduces Fehling's solution and silver solutions; the *chloride* and *sulphate* crystallise in flakes and are only slightly soluble in water.

Benzylidenefluorylhydrazine, $C_{13}H_9\cdot NH\cdot N{:}CHPh$, crystallises from ethyl acetate in yellowish, glistening tablets, sinters at 182°, and melts at about 188°. *Furfurylidenefluorylhydrazine*, $C_{13}H_9\cdot NH\cdot N{:}C_5H_4O$, crystallises from ethyl acetate in glistening, brownish flakes, and melts at 190—191° (corr.). *β-Propylidenefluorylhydrazine*, $C_{13}H_9\cdot NH\cdot N{:}CMe_2$, crystallises from hot alcohol in brownish tablets, sinters at 125°, and melts at 137—138° (corr.). *Ethyl acetoacetate fluorylhydrazone*, $C_{19}H_{20}O_2N_2$, crystalllises from alcohol in glistening, yellowish needles and melts at 124° (corr.).

2-Nitrofluorenone,  $CO<\begin{array}{l}C_6H_4\\ |\\ C_6H_3\cdot NO_2\end{array}$, previously obtained by nitrating diphenylene ketone, can also be prepared by oxidising nitrofluorene with acetic acid and potassium dichromate. 2-*Aminofluorenone*,  $CO<\begin{array}{l}C_6H_4\\ |\\ C_6H_3\cdot NH_2\end{array}$, prepared by reducing the preceding compound with ammonia and hydrogen sulphide, crystallises from alcohol in deep violet-red, stout, glistening prisms, sinters at 156°, melts at 163° (corr.) to a deep-red liquid, is insoluble in water, but soluble in most organic solvents; the *hydrochloride*, $C_{13}H_9ON_8,HCl$, crystallises from acid solution in glistening, yellowish prisms, reddens a pine splinter, and is decomposed by water. The *phenylhydrazone*, $C_{19}H_{15}N_3$, forms golden-yellow crystals, sinters at about 138° and melts at about 148° (corr.).

4-*Aminodiphenylcarboxylic acid*, $NH_2\cdot C_{12}H_8\cdot CO_2H$, prepared by fusing aminofluorenone with potassium hydroxide, crystallises from hot water or alcohol in colourless needles and melts at about 215°.

2-*Diazofluorenone chloride* forms small, glistening, yellow needles, decomposes at 128°, and crystallises from hot water, but is decomposed by boiling. 2-*Hydroxyfluorenone*, $C_{18}H_8O_2$, crystallises from dilute acetic acid in glistening, alizarin-red needles, sublimes below the melting point, sinters at 200°, melts at 210—211° (corr.), dissolves in alkalis and less readily in ammonia. *2-Aminofluorene alcohol*, $C_{13}H_{11}ON$, prepared by reducing an alcoholic solution of nitrofluorenone with zinc dust and calcium chloride, crystallises from hot alcohol in colourless, iridescent needles, sinters at 192°, and melts at 200° (corr.); the *hydrochloride*, *nitrate*, and *sulphate* crystallise in prisms. T. M. L.

Action of *iso*Butylene Dibromide on Benzene in the presence of Aluminium Chloride. By F. Bodroux (*Compt. rend.*, 1901, **132**, 1333—1336. Compare this vol., i, 196).—*iso*Butylene dibromide, acting on benzene in the presence of aluminium chloride, gives rise to *a-phenyl-β-methylpropane*, $CH_2Ph{\cdot}CHMe_2$, *aβ-diphenyl-β-methylpropane*, $CH_2Ph{\cdot}CMe_2Ph$, and a small amount of a substance crystallising from alcohol in colourless prisms and melting at 128°.

The first of these hydrocarbons is a colourless liquid having an agreeable odour and boiling at 171—173° under a pressure of 750 mm.; its constitution is determined by treating it with excess of bromine and aluminium, bromide when it gives rise to *nonabromo*iso*butylbenzene*, $C_6Br_5{\cdot}C_4H_5Br_4$, melting at 216—217°, and a small amount of hexabromobenzene. Under these conditions, the isomeride, CMe_3Ph, yields only hexabromobenzene.

The second hydrocarbon is a pale yellow liquid having a blue fluorescence; it boils at 284—287° under 750 mm. pressure, and has a sp. gr. 0·984 at 15°. When treated with excess of bromine and aluminium bromide, the compound undergoes fission at the quaternary carbon atom, and yields a mixture of nonabromo*iso*butylbenzene and hexabromobenzene. G. T. M.

Direct Production of Aromatic Amines from the Hydrocarbon. By Carl Graebe (*Ber.*, 1901, **34**, 1778—1781).—Aniline is produced in small quantities by the action of hydroxylamine on benzene in presence of aluminium or ferric chloride, but not in presence of zinc chloride. Toluene gives a mixture of *p*-toluidine with a little *o*-toluidine, *o*-xylene gives a relatively good yield of 4-amino-1 : 2-xylene; *m*-xylene gives 4-amino-1 : 3-xylene, and *p*-xylene gives a small amount of 2-amino-1 : 4-xylene. Mesitylene is partially converted into mesidine. Naphthalene gives a small yield of *a*- and *β*-naphthylamines.

Phenylhydroxylamine, *p*-tolylhydroxylamine, and benzophenoneoxime undergo secondary changes when heated with benzene and aluminium chloride, and do not yield any appreciable quantity of condensation product. T. M. L.

Oxidising Action of Mercury Fulminate on Dimethylaniline. By Roland Scholl and E. Bertsch (*Ber.*, 1901, **34**, 2036—2039).—Tetramethyl-4 : 4′-diaminodiphenylmethane and a yellow *base*,

$$C_{20}H_{24}O_2N_4,$$

are produced when mercuric fulminate reacts with dimethylaniline at 160—170°. The yellow base is sparingly soluble in alcohol, and is best purified by solution in chloroform and precipitation with ether; it melts at 208°, and is readily soluble in chloroform or acetone.

The *hydrochloride*, $C_{20}H_{24}O_2N_4,2HCl$, forms colourless crystals, the *picrate*, $C_{20}H_{24}O_2N_4,2C_6H_3O_7N_4$, yellow needles melting at 192°, the *platinichloride*, yellowish-red needles, the *mercurichloride*,

$$C_{20}H_{24}O_2N_4,2HCl,HgCl_2,$$

colourless needles. The base does not react with phenylhydrazine or hydroxylamine, but on treatment with nitrous acid yields a mixture of two isomeric *dinitro*-derivatives. The α-compound melts at 201—202° and is readily soluble in chloroform or acetone; the β-derivative forms yellow needles, melts at 225°, and is sparingly soluble in chloroform containing a little alcohol. J. J. S.

Formation of Chains. LV. Derivatives of Phenoxyacetamide and -anilide. By Carl A. Bischoff [and, in part, with J. Bloch, S. Gerbert, F. Mitt, A. Pessis, and S. Werschow] (*Ber.*, 1901, **34**, 1835—1843).—The reactions between sodium phenoxide and α-bromo-derivatives of the fatty acid amides in indifferent solvents have been studied quantitatively. When heated until the products give a neutral reaction, more than 90 per cent. of the α-condensation product is obtained in each case. When warmed for 1 hour in benzene solution, the quantities obtained, calculated from the amount of sodium bromide formed, were with: α-bromopropionamide, 95—96; α-bromopropionanilide, 27—30; α-bromobutyramide, 92—95; α-bromobutyranilide, 16—19; α-bromo*iso*butyramide, 64; α-bromo*iso*butyranilide, 32—33; α-bromo*iso*valeramide, 37—39; α-bromo*iso*valeranilide, 16 per cent. α-Bromopropionamide distils at 135° under 19 mm. pressure, and the product obtained by the action of sodium phenoxide is identical with Saarbach's α-phenoxypropionamide (Abstr., 1879, 642). α-Phenoxybutyramide melts at 123°, and not at 111° as stated by Luchmann (Abstr., 1896, i, 544). α-Bromo*iso*butyramide distils at 145° under 17 mm. pressure; *α-phenoxy*iso*butyramide* crystallises in alcohol in stout needles melting at 114°. *α-Phenoxy*iso*valeramide* crystallises in felted needles melting at 143°. α-Phenoxyacetanilide obtained from sodium phenoxide and chloroacetanilide melts at 101·5°; Morel (*Bull. Soc. Chim.*, 1899, [iii], **21**, 964) gives 99—100°. α-Bromopropionylanilide distils at 186° under 19 mm. pressure, and *α-phenoxypropionylanilide*,

OPh·CHMe·CO·NHPh,

crystallises from light petroleum in rhombic plates melting at 118·5—119°, and distilling at 211—212° under 14 mm. pressure; it may also be prepared by the action of aniline on α-phenoxypropionylchloride, which distils at 146—147° under 55 mm. pressure. *α-Phenoxybutyranilide*, OPh·CHEt·CO·NHPh, crystallises in colourless needles melting at 93—94°. *α-Phenoxy*iso*butyranilide* also melts at 93° and distils at 210—211° under 16 mm. pressure; when hydrolysed with alcoholic potash and a little water, it yields α-phenoxy*iso*butyric acid, the chloride of which cannot be distilled under reduced pressure without decomposition. *α-Phenoxy*iso*valeranilide* crystallises in branching needles melting at 97°. J. J. S.

Formation of Chains. LVI. Toluidides and Naphthalides of Phenoxy-fatty Acids. By Carl A. Bischoff (*Ber.*, 1901, **34**, 1844—1854. Compare preceding abstract).—The compounds described have been obtained by the action of sodium phenoxide on the toluidides and naphthalides of brominated fatty acids.

[With L. KONKOROWITSCH.]—*a-Phenoxypropionyl*-o-*toluidide* crystallises from alcohol in colourless needles melting at 88—90°; *a-phenoxybutyryl*-o-*toluidide* melts at 101—102°. *a*-Bromo*iso*butyryl-*o*-toluidide cannot be distilled under reduced pressure without decomposition; on treatment with sodium phenoxide, it yields both *a*- and *β-phenoxy*iso*butyryl-*o*-toluidides*, melting respectively at 62° and 91°, but no toluidide of methacrylic acid. *a-Phenoxy*iso*valeryl*-o-*toluidide* crystallises in needles and melts at 116—117°.

[With N. GOLDBLATT.]—*a-Phenoxypropionyl*-m-*toluidide* crystallises in hexagonal plates melting at 86·5° and distilling at 220° under 15 mm. pressure. *a-Phenoxybutyryl*-m-*toluidide* forms prismatic needles melting at 92·5°, and the iso*butyryl* compound cruciform needles melting at 83°. *a-Phenoxy*iso*valeryl*-m-*toluidide* melts at 89—90.°

[With J. LIEBERMANN.]—*a-Phenoxypropionyl*-p-*toluidide* melts at 115°, the *butyryl* compound at 124°, the iso*butyryl* compound also at 124°, and the iso*valeryl* compound at 122°.

[With S. GERBERT.]—The percentage amounts of the substances which have reacted at the end of an hour are the same for the *m*- and *p*-propionyl and *iso*valeryl compounds. With *iso*butyryl compounds, the ortho-derivative more readily reacts, and with butyryl compounds, the meta-derivative less readily than the ortho and para.

[With P. MESCHLUMJANZ.] — *a-Phenoxypropionyl-a-naphthalide*, $OPh\cdot CHMe\cdot CO\cdot NH\cdot C_{10}H_7$, crystallises in small needles, melts at 131°, and distils at 260° under 20 mm. pressure; it is only sparingly soluble in ether or light petroleum. The *butyryl* compound melts at 148° and distils at 260° under 15 mm. pressure, the iso*butyryl* compound crystallises in prisms melting at 98°, and the iso*valeryl* compound in needles melting at 102°.

[With J. FEIGIN.]—*a-Phenoxypropionyl-β-naphthalide* melts at 117°, the *butyryl* compound also at 117°; the iso*butyryl* at 157·5°, and the iso*valeryl* at 128°.

In all cases, the *β*-derivatives are formed less readily than the isomeric *a*-compounds. J. J. S.

Formation of Chains. LVII. Nitroanilides of Phenoxyfatty Acids. By CARL A. BISCHOFF [and, in part, with S. GERBERT, S. HIRSCHFELD, K. KRAUSE, F. MITT, and A. WATSCHJANZ] (*Ber.*, 1901, **34**, 2057—2069).—*a-Phenoxypropionyl-o-nitroanilide*,

$$OPh\cdot CHMe\cdot CO\cdot NH\cdot C_6H_4\cdot NO_2,$$

crystallises in yellowish, stout prisms or needles, melts at 88°, distils at 248° under 28 mm. pressure, and is readily soluble in most solvents. *a-Phenoxybutyryl*-o-*nitroanilide* was only obtained in the form of an impure oil. The iso*butyryl* compound crystallises from light petroleum in lemon-yellow needles, melts at 71°, distils at 236—237° under 17 mm. pressure, and is readily soluble. *a-Phenoxy*iso*valeryl*-o-*nitroanilide* was obtained in the form of an oil from which well-developed, flat plates melting at 47° separated. The following isomeric *m*- and *p*-compounds have also been prepared:

	Meta.	Para.
	m.p.	m.p.
Propionyl	118° prisms.	141—142° prisms.
Butyryl	81° plates.	108° minute needles.
*iso*Butyryl	119° needles.	182° needles.
*iso*Valeryl	77° plates.	125° needles.

Most of the compounds have been prepared both by the action of sodium phenoxide on the nitroanilides of α-bromo-fatty acids, and also by the action of nitroanilines on the acid chlorides of phenoxy-fatty acids. The products obtained by the former method were often oily and did not admit of purification. By the reaction of sodium phenoxide on α-bromo*iso*butyryl-*p*-nitroanilide in benzene, a small amount of *β-phenoxy*iso*butyryl-*p*-nitroanilide*, $\mathrm{OPh{\cdot}CH_2{\cdot}CHMe{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2}$, was also obtained. It forms glistening, pale-yellow plates melting at 109°.

A tabulated statement is given of the yields obtained by heating together equivalent quantities of sodium phenoxide and the respective bromo-fatty nitroanilides for 1 hour in benzene. J. J. S.

Formation of Chains. LVIII. Reaction of Sodium Phenoxide with Derivatives of α-Bromo-fatty Acids and Methyl- and Ethyl-aniline. By CARL A. BISCHOFF [and in part J. BLOCH, A. PESSIS, and S. WERSCHOW] (*Ber.*, 1901, **34**, 2125—2135. Compare preceding abstract).—*Chloroacetylmethylanilide*,

$$\mathrm{CH_2Cl{\cdot}CO{\cdot}NMePh},$$

prepared from methylaniline and chloroacetyl chloride, crystallises in prismatic plates melting at 48°, the corresponding *bromo*-derivative forms prismatic plates melting at 69°. *Phenoxyacetylmethylanilide*, $\mathrm{OPh{\cdot}CH_2{\cdot}CO{\cdot}NMePh}$, prepared by boiling mol. proportions of either of the foregoing substances and sodium phenoxide in solution in toluene, crystallises in right angled plates melting at 94°. *α-Phenoxypropionylmethylanilide*, OPh·CHMe·CO·NMePh, prepared from α-bromopropionylmethylanilide and sodium phenoxide (yield 81 per cent.), crystallises in rhombic plates melting at 57·5° and boiling at 206° under 18 mm. pressure. By the action of sodium phenoxide on bromobutyrylmethylanilide, the expected phenoxyanilide was not obtained, but a mixture of phenol and crotonylmethylanilide. *α-Phenoxybutyryl chloride*, OPh·CHEt·COCl, prepared from the corresponding acid and phosphorus pentachloride, is a colourless oil boiling at 128—131° under 38 mm. pressure. *α-Phenoxybutyrylmethylanilide*, obtained from methylaniline and the last-mentioned compound, is a viscous oil boiling at 245—248° under 69 mm. pressure.

From α-bromo*iso*butyrylmethylanilide and sodium phenoxide is obtained a product which, on fractionation under pressure, is resolved into *α-methylacrylmethylanilide*, $\mathrm{CH_2{:}CMe{\cdot}CO{\cdot}NMePh}$, prismatic plates melting at 57° and boiling at 177° under 33 mm. pressure, and *α-phenoxy*iso*butyrylmethylanilide*, $\mathrm{OPh{\cdot}CMe_2{\cdot}CO{\cdot}NMePh}$, a colourless oil boiling at 210—211° under 24 mm. pressure. The latter substance could not be prepared from methylaniline and α-phenoxy*iso*butyryl chloride. α-Bromo*iso*valerylmethylanilide and sodium phenoxide yield, together with a mixture of phenols, *ββ-dimethylacrylmethylanilide*, $CMe_2\colon CH\cdot CO\cdot NMePh$, which forms a colourless oil boiling at 166—168° under 36 mm. pressure.

α-Phenoxypropionylethylanilide, $OPh\cdot CHMe\cdot CO\cdot NEtPh$, prepared from α-bromopropionylethylaniline and sodium phenoxide, crystallises in rhombic prisms melting at 47·5°. *Acrylethylanilide*,

$$CH_2\colon CH\cdot CO\cdot NEt\cdot Ph,$$

is obtained as a by-product and forms an oil boiling at 150—160° under 17 mm. pressure.

From α-bromobutyrylethylaniline and sodium phenoxide, *crotonylethylanilide*, $CHMe\colon CH\cdot CO\cdot NEtPh$, and a small quantity of *α-phenoxybutyrylethylanilide* are obtained. The former is an oil boiling at 167—168° under 11—12 mm. pressure, the latter boils at about 210—220° under the same pressure, but was not obtained in a pure state.

α-Methylacrylethylanilide, $CH_2\colon CMe\cdot CO\cdot NEtPh$, is the only product of the interaction of α-bromo*iso*butyrylethylanilide and sodium phenoxide, and forms an oil boiling at 161° under 20 mm. pressure. *ββ-Dimethylacrylethylanilide*, $CMe_2\colon CH\cdot CO\cdot NEtPh$, obtained by the action of sodium phenoxide on α-bromo*iso*valerylethylanilide, boils at 165° under 18 mm. pressure.

It is seen that an increase in length of the carbon chain of the acyl group decreases the amount of phenoxy-derivatives and promotes the formation of derivatives of acrylic acid. K. J. P. O.

Formation of Chains. LIX. Reaction of Sodium Phenoxide with Derivatives of α-Bromo-fatty Acids and Benzaniline, Diphenylamine, and Carbazole. By CARL A. BISCHOFF [and in part P. DENISSENKO, S. GERBERT, W. KISSIN, and F. MITT] (*Ber.*, 1901, **34**, 2135—2145).—*α-Phenoxypropionylbenzylanilide*,

$$OPh\cdot CHMe\cdot CO\cdot NPh\cdot C_7H_7,$$

prepared from α-bromopropionylbenzylanilide and sodium phenoxide, crystallises in lustrous prisms melting at 111—112°. α-Bromobutyrylbenzylanilide and sodium phenoxide yield mainly *crotonylbenzylanilide*, $CHMe\colon CH\cdot CO\cdot NPh\cdot C_7H_7$, forming colourless crystals melting at 82°, and a small quantity of *α-phenoxybutyrylbenzylanilide*, which was also obtained by the action of α-phenoxybutyryl chloride on benzylaniline, and crystallises in needles melting at 65° and boiling at 245° under 15 mm. pressure. *α-Phenoxy*iso*butyrylbenzylanilide*,

$$OPh\cdot CMe\cdot CO\cdot NPh\cdot C_7H_7,$$

could only be prepared from the acid chloride and the base, and crystallises in large, prismatic plates melting at 52—53°. By the action of sodium phenoxide on α-bromo*iso*butyrylbenzylanilide only *methylacrylbenzylanilide* is obtained. The latter substance forms an oil boiling at 204° under 15 mm. pressure. *α-Phenoxy*iso*valerylbenzylanilide*, $OPh\cdot CHPr^\beta\cdot CO\cdot NPh\cdot C_7H_7$, is similarly only procurable from the acid chloride and the base, and crystallises in right angled plates melting at 67°. From α-bromo*iso*valerylbenzylanilide and sodium phenoxide, *ββ-dimethylacrylbenzylanilide* is formed as a yellowish oil boiling at 226° under 20 mm. pressure. *α-Phenoxypropionyldiphenylamide*, $OPh\cdot CHMe\cdot CO\cdot NPh_2$, prepared by the action of sodium phenoxide on α-bromopropionyldiphenylamide, crystallises in long, colourless prisms melting at 93°. The corresponding butyryl compound could not be obtained from α-bromobutyrylphenylamide; *crotonyldiphenylamide*, $CHMe{:}CH{\cdot}CO{\cdot}NPh_2$, was the only product, and formed small prisms melting at 115—116°. *α-Phenoxybutyryldiphenylamide*, prepared from diphenylamine and α-phenoxybutyryl chloride, crystallises in colourless leaflets melting at 67°. α-Bromo*iso*butyryldiphenylamide and sodium phenoxide yield only *α-methylacryldiphenylamide*, which crystallises in right angled plates or needles melting at 108°. The phenoxy-compound was not formed, neither could it be prepared from α-phenoxy*iso*butyryl chloride and diphenylamine. Similarly, *ββ-dimethylacryldiphenylamide*, $CMe_2{:}CH{\cdot}CO{\cdot}NPh_2$, is alone produced from sodium phenoxide and α-bromo*iso*valeryldiphenylamide and forms needles melting at 99°.

α-Bromo-, propionyl, butyryl, and *iso*valeryl derivatives of carbazole only react with sodium phenoxide when heated in boiling nitrobenzene. In all cases, sodium bromide and carbazole were the only products isolated.

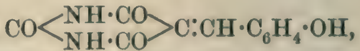
The results in this and previous papers are discussed.

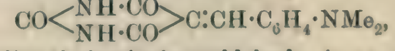
K. J. P. O.

Reduction of Phenylthiocarbimide. By ALEXANDER GUTBIER (*Ber.*, 1901, **34**, 2033—2034).—When reduced in acid solution, thiocarbimides yield primary amines and thioformaldehyde, but phenylthiocarbimide, when reduced with aluminium amalgam in neutral solution, yields *s*-diphenylthiocarbamide and methyl mercaptan, the latter being probably formed by the reduction of thioformaldehyde which is first produced.

J. J. S.

Condensation of Barbituric Acid with Aromatic Aldehydes to Coloured Substances. By ARTHUR WEINSCHENK (*Ber.*, 1901, **34**, 1685—1687).—Barbituric acid, which with ortho-substituted benzaldehydes (Conrad and Reinbach, this vol., i, 410) yields colourless substances, with para-substituted derivatives yields coloured products.

p-*Hydroxybenzylidenebarbituric acid*,

$CO{<}\begin{matrix}NH{\cdot}CO\\NH{\cdot}CO\end{matrix}{>}C{:}CH{\cdot}C_6H_4{\cdot}OH$,
prepared by using *p*-hydroxybenzaldehyde, crystallises from alcohol in canary-yellow, microscopic prisms, and does not melt at 300°; with dilute potassium hydroxide, it yields a reddish-yellow *potassium* salt, but is readily resolved into its components by an excess of the alkali. p-*Dimethylaminobenzylidenebarbituric acid*,


$$CO{<}\begin{matrix}NH{\cdot}CO\\NH{\cdot}CO\end{matrix}{>}C{:}CH{\cdot}C_6H_4{\cdot}NMe_2,$$

obtained from *p*-dimethylaminobenzaldehyde, is an orange-red, crystalline powder which sinters at 270° and melts and decomposes at 282°; the *hydrochloride* forms stellate aggregates of orange coloured needles.

W. A. D.

Action of *p*-Xylylene Bromide on some Primary, Secondary, and Tertiary Amines and Alkaloids. By WAHAN MANOUKIAN (*Ber.*, 1901, **34**, 2082—2092).—*p*-Xylylene bromide differs in some respects from *o*-xylylene bromide (Scholtz, Abstr., 1898, i, 305) in its action on amines. It does not yield ring compounds of the type of dihydro*iso*indole with primary amines, and does not form ammonium bromides with secondary amines.

p-*Xylylenedi-a-naphthylamine*, $C_6H_4(CH_2\cdot NH\cdot C_{10}H_7)_2$, obtained by the action of *p*-xylylene bromide on *a*-naphthylamine in chloroform solution, is a white, crystalline powder melting at 165°. p-*Xylylenediisobutylamine* crystallises in large prisms melting at 65°; the *platinichloride* crystallises in large red prisms melting at 220°; the *aurichloride* forms slender needles melting at 205°; and the *picrate* melts at 171°. p-*Xylylenedidiphenylamine*, $C_6H_4(CH_2\cdot NPh_2)_2$, crystallises in small, light green needles melting at 186°. p-*Xylylenedipiperidine* crystallises in transparent leaflets melting at 86°; the *platinichloride* decomposes at about 250°; the *aurichloride* crystallises in large, yellow needles melting at 215°, and the *picrate* melts at 221°. p-*Xylyleneditriethylammonium bromide*, $C_6H_4(CH_2\cdot NEt_3Br)_2$, is formed by the direct combination of *p*-xylylene bromide with triethylamine, and crystallises in large, colourless needles melting at 230°; the *perbromide*, $C_6H_4(CH_2\cdot NEt_3Br_3)_2$, is an orange-yellow precipitate which melts at 164°; the *platinichloride* crystallises in orange coloured prisms melting at 238°, and the *aurichloride* crystallises in yellow needles melting at 242°. p-*Xylyleneditripropylammonium bromide* forms small needles melting at 223°; the *perbromide* melts at 181—182°; the *platinichloride* melts at 235°, and the *aurichloride* at 214°. p-*Xylylenedipyridinium bromide* crystallises in small needles melting at 260°; the *perbromide* melts at 149°, the *platinichloride* at 253°, and the *aurichloride* at 246°. p-*Xylylenediquinolinium bromide* crystallises in pale violet, microscopic needles melting at 306°; the *perbromide* melts at 206°, the *platinichloride* at 257°, and the *aurichloride* at 242°. With strychnine, *p*-xylylene bromide yields p-*xylylenedistrychninium bromide*, which crystallises in microscopic needles melting at 291°; the *perbromide* melts at 195°, the *platinichloride* at 247—249°, and the *aurichloride* at 210°. Morphine and quinine, on the other hand, yield mixtures of the monoammonium and diammonium compounds, which cannot easily be separated into their constituents.

A. H.

Action of Methyl on the Velocity of Reaction of the β-Aromatic Hydroxylamines. By Eugen Bamberger and Adolf Rising (*Annalen*, 1901, **316**, 257—292. Compare Abstr., 1898, i, 20).—The formation of an azoxy-derivative by the interaction of a β-aromatic hydroxylamine with the corresponding nitroso-compound has been employed in studying the influence of the orientation of substituent methyl radicles on the velocity of reaction. The reagents were mixed in alcoholic solutions maintained at 15·2—15·3°, and from time to time samples were taken and tested with Fehling's solution, the amount of reduction being a measure of the quantity of unaltered hydroxylamine derivative. The compounds containing no methyl groups, or having these substituents in meta-positions, react most rapidly, the para-substituted derivatives are much less active, and the ortho-substituted derivatives are affected least of all. The three tolylhydroxylamines and the corresponding nitroso-compounds were employed in demonstrating this generalisation. The rule applies also to the xylene compounds, 1 : 3-xylyl-2-hydroxylamine being the least active of any of these derivatives.

2-*Azoxy*-1 : 3-*xylene* is obtained in small yield when 1 : 3-xylyl-2-hydroxylamine is boiled for 12 hours with an alcoholic solution of 2-nitroso-1 : 3-xylene; it crystallises in straw-yellow needles melting at 88·5—89° and is readily soluble in the ordinary organic solvents. Mesitylhydroxylamine and nitrosomesitylene, which contain methyl groups both in the para- and in the two ortho-positions, do not exhibit any tendency to undergo condensation.

1 : 2-*Xylene*-4-*hydroxylamine*, prepared by reducing 4-nitro-1 : 2-xylene with zinc dust in the presence of a dilute alcoholic solution of ammonium chloride, crystallises from benzene in white needles melting at 98—101°. It readily dissolves in ether, alcohol, acetone, or light petroleum, and its solution in these solvents, when maintained for several hours at the boiling point, yields a mixture of 4-amino-1 : 3-xylene and the corresponding azoxyxylene. 4-*Nitroso*-1 : 3-*xylene*, obtained either as an intermediate product in the preceding experiments or by oxidising 1 : 2-xylene-4-hydroxylamine with a cold solution of ferric chloride, crystallises from alcohol in light bluish-green needles melting at 44—45°; when dried for 12 days on porous plates, the green crystals become yellow; the melting point, however, remains unaltered, and the green colour is recovered on distilling the product in steam.

4-*Azoxy*-1 : 2-*xylene* crystallises from light petroleum in light canary-yellow needles and melts at 140—140·5°.

1 : 2-*Xylyl*-3-*hydroxylamine* crystallises in snow-white leaflets and melts at 74°, the yield of the base from the corresponding nitro-compound being 55—60 per cent.

3-*Nitroso*-1 : 2-*xylene* crystallises in white needles and melts at 91—91·5°, at the same time becoming green in colour; the corresponding azoxy-compound is obtained in lustrous, almost colourless needles and melts at 116·5°.

1 : 4-Xylyl-3-hydroxylamine crystallises in white needles and melts at 91·5°; it is soluble in the ordinary organic solvents, with the exception of light petroleum; the corresponding *nitroso*-compound crystallises in white, silky needles melting at 101·5°; the *azoxy*-compound is prepared either by the interaction of the two preceding compounds, or from the hydroxylamine, either by atmospheric oxidation in aqueous solution, or by heating the base on the water-bath, in the latter case being accompanied by *p*-xylidine; when absolutely pure, it is colourless, but in general forms pale yellow, lustrous needles melting at 110—110·5°.

On digesting the aromatic hydroxylamines with dilute sulphuric acid (1 : 15) at 15°, those containing methyl groups in the ortho-position with respect to the nitrogen atom are most readily decomposed; phenylhydroxylamine and 1 : 3-xylyl-2-hydroxylamine require for their complete decomposition 8 days and 6 minutes respectively, whilst mesitylhydroxylamine is destroyed instantaneously. The paper also contains details of the preparation of the tolylhydroxylamines and the corresponding nitroso-compounds; *o*-tolylhydroxylamine, formerly described as an oil (Abstr., 1895, i, 217), is found to melt at 44°.

The orientation of the substituent methyl groups exerts a very marked influence on the interaction of the aromatic hydroxylamines with benzenediazonium chloride. The reaction was in each case carried out in alcoholic solution at 0°, the time allowed for the experiment being 80 minutes. Under these conditions, a yield of 98·5 per cent. of benzeneazohydroxyanilide is obtained from phenylhydroxylamine; *m*-tolylhydroxylamine yields 96·6 per cent. of benzeneazohydroxy-*m*-toluidide, which melts at 125·5°. Benzeneazohydroxy-*p*-toluidide, melting at 124°, is obtained in a similar manner from *p*-tolylhydroxylamine, the yield being 90·3 per cent.; in the case of benzeneazohydroxy-*o*-toluidide (Abstr., 1899, i, 687), the yield is 75 per cent. 4-*Benzeneazohydroxy*-1 : 2-*xylidide* melts at 140—141°, the yield is 95·5 per cent.; 2-*benzeneazohydroxy*-1 : 4-*xylidide*, 3-*benzeneazohydroxy*-1 : 2-*xylidide*, 4-*benzeneazohydroxy*-1 : 3-*xylidide*, and 2-*benzeneazohydroxy*-1 : 3-*xylidide* melt at 111·5°, 105°, 82·5—83°, and 113° respectively, the yields of these compounds obtained by the general method being 79·2, 76·7, 51·9, and 31·1 per cent. respectively. All these azohydroxyamides crystallise in yellow needles, and yield characteristic insoluble, brownish-yellow copper derivatives. It will be seen that 2-benzeneazohydroxy-1 : 3-xylidide, which contains 2 methyl groups in the ortho-position with respect to the nitrogen atom, reacts least readily with the diazonium salt; when the para-position is also substituted, as in mesitylhydroxylamine, there is no interaction whatever, the latter base merely becoming oxidised, and yielding a small amount of nitrosomesitylene. G. T. M.

1 : 3-Xylyl-2-hydroxylamine and 2-Nitroso-1 : 3-xylene. By EUGEN BAMBERGER and ADOLF RISING (*Annalen*, 1901, **316**, 292—311. Compare preceding abstract).—1 : 3-Xylene-2-hydroxylamine (compare von Pechmann, Abstr., 1898, i, 310), prepared by reducing 2-nitro-1 : 3-xylene in alcoholic solution with zinc dust in the presence of ammonium chloride, crystallises in white, lustrous needles, and melts at 97—98·5°; it readily dissolves in the ordinary solvents, with the exception of light petroleum. The preceding base, when suspended in water and oxidised by a current of air, yields 2-*amino*-4-*hydroxy*-1 : 3-*xylene*, a substance crystallising from water or chloroform in lustrous needles melting at 180·5—181·5°, together with 2-nitroso-1 : 3-xylene (m. p. 141·5°), 1 : 3-xyloquinone, 1 : 3-xylidine, and a *compound* crystallising in white prisms and melting at 189°. 2-*Amino*-4-*hydroxy*-1 : 3-*xylene*, when dissolved in aqueous sodium hydroxide, yields at first a colourless solution, which becomes violet on exposure to air and on boiling evolves ammonia; when shaken with an alkaline solution of α-naphthol, a transient indophenol coloration is observed; the aminophenol yields, with salicylaldehyde, a copious, yellow precipitate, but does not give any colour reaction with ferric chloride. The *sulphate*, $C_8H_{11}NO,\frac{1}{2}H_2SO_4$, crystallises in white, lustrous needles and melts at 268°; when its solution is boiled, hydrolysis takes place, resulting in the formation of 2 : 5-dihydroxy-1 : 3-xylene.

2-Nitroso-1 : 3-xylene and nitrosomesitylene differ from their lower homologues in not possessing the characteristic irritating odour of nitrosobenzene ; the colours of their solutions vary perceptibly with the temperature ; this phenomenon is probably due to changes in the state of aggregation of the dissolved molecules. The cryoscopic molecular weight determination in benzene points to the existence of double molecules, and the ebullioscopic method indicates a certain degree of association, even in boiling acetone.

1 : 3-Xylyl-2-hydroxylamine, when treated with cold dilute sulphuric acid yields, in addition to the substances obtained by its atmospheric oxidation, 2-*amino*-5-*hydroxy*-1 : 3-*xylene*-4-*sulphonic acid*, and 2 : 2′-*diamino*-1 : 3-*xylyl* 5-*oxide*. The former of these products crystallises from water in lustrous, white needles, which, on treatment with alkaline α-naphthol solution, give an indophenol reaction ; when boiled with a solution of sodium acetate, the sodium salt is produced, the reaction being a reversible one. The sulphonic acid, when heated with dilute hydrochloric acid at 160°, loses its sulphonic group, and becomes converted into 2-amino-5-hydroxy-1 : 3-xylene ; at the same time, a portion of the latter compound undergoes further hydrolysis, resulting in the elimination of ammonia and the formation of 2 : 5-dihydroxy-1 : 3-xylene.

2 : 2′-Diamino-1 : 3-xylyl 5-oxide forms colourless, highly refractive needles or plates melting at 156·7—157° ; its *hydrochloride* crystallises in leaflets melting at 320°, and furnishes a characteristic colour reaction with ferric chloride, the colour changing from violet to yellow, a red precipitate being formed at an intermediate stage ; the mixture, on boiling, evolves 1 : 3-xyloquinone. The base, when diazotised, yields red azo-compounds with the naphthols ; its *acetyl* derivative, obtained by the action of acetic anhydride on the water-bath, crystallises from alcohol in white, silky needles and melts at 283°.

1 : 3-Xylyl-2-hydroxylamine is very stable towards sodium hydroxide solution in the absence of air, and after 14 days only 4 per cent. of the base is converted into the corresponding nitroso-xylene ; in the presence of oxygen, the oxidation follows the products previously indicated. G. T. M.

Acidimetric Value (Avidity) of *p*-Sulphanilic Acid. By Gustave Massol (*Compt. rend.*, 1901, 132, 1572—1573).—The heats of dissolution and neutralisation of anhydrous *p*-sulphanilic acid are −3·84 and 9·07 Cal. respectively, and the heats of dissolution of the dihydrated and anhydrous sodium salt are −7·84 and −1·64 Cal. respectively, the heat of hydration of the anhydrous compound being 3·34 Cal., and its heat of formation 18·08 Cal.

The heats of neutralisation of sulphurous, phenylsulphonic and *p*-sulphanilic acids are compared with those of carbonic, benzoic, and *p*-aminobenzoic acids, the diminution in avidity (measured in heat units), due to the introduction of amidogen, is 4·53 Cal. in the former case, and 1·37 Cal. in the latter.

In solution, *p*-aminobenzoic acid has a greater avidity than *p*-sulphanilic acid, the values being 12·12 and 9·07 Cal. respectively ; in the solid state, however, the latter acid is stronger, the corresponding values for the heats of neutralisation being 16·18 and 18·08 Cal.

G. T. M.

Hydrolysis of Phenol Ethers by Alcoholic Potash. By Richard Stoermer and Bruno Kahlert (*Ber.*, 1901, **34**, 1812).—The authors find, in contradiction to the statement of Bouveault (Abstr., 1899, i, 437), that the ethers of monoatomic phenols are hydrolysed by alcoholic potash, provided that the temperature be high and the time of action long. Anisole and phenetole both yield phenol when treated in this way for 15 hours at 180—200°. Anethole in the same way yields anol.

A. H.

Action of Phenols on Ethylic Oxalate. By J. Bishop Tingle and Leo O'Byrne (*Amer. Chem. J.*, 1901, **25**, 496—501).—By the action of ethyl oxalate on thymol in presence of sodium, J. B. and A. Tingle (*Amer. Chem. J.*, 1899, **21**, 261) obtained an oily condensation product which gives a dark red coloration with ferric chloride. The behaviour of the following substances under similar circumstances has been investigated: catechol, carvacrol, picric acid, β-naphthol, ethyl salicylate, quinone, guaiacol, resorcinol, phloroglucinol, quinol, anisole, and carvol. The first six of these showed no evidence of having reacted, whilst guaiacol yielded only tarry products. Resorcinol furnished a yellow, crystalline substance, which melts and decomposes at 257—258°, and is perhaps identical with the compound obtained by Michael (Abstr., 1887, 949) by the interaction of resorcinol, ethyl oxalate, and sodium ethoxide. Phloroglucinol yielded a crystalline compound which softens at 305°, together with another substance which crystallises in plates and blackens without melting at 240°. With quinol, a substance was produced which blackens above 200° and remains unmelted at 300°. Anisole and carvol form oily condensation products, similar to that obtained from thymol, which give a deep red coloration with ferric chloride and alcohol; the substance prepared from carvol furnishes barium and copper salts, which, like the parent substance, readily become resinous; the resin has a strong odour of violets.

E. G.

Ethers of *p*-Aminophenol and their Carbamide Derivatives. By Leopold Spiegel and S. Sabbath (*Ber.*, 1901, **34**, 1935—1947).—The ethers of *p*-aminophenol are all very poisonous and of no therapeutic value (differing from the acetyl derivative of the ethyl ether, "phenacetin"), also the carbamide derivatives have no sweet taste like *p*-phenetole- and *p*-anisole-carbamides ("dulcin").

The ethers of *p*-aminophenol are easily obtained by the reduction with tin and hydrochloric acid of the corresponding nitro-compounds, which are prepared by the action of halogen alkyls on potassium *p*-nitrophenoxide. The carbamide derivatives are best prepared by warming on a water-bath aqueous solutions of carbamide and the hydrochlorides of the amino-ethers, the thiocarbamides being obtained in a similar manner from ammonium thiocyanate. At higher temperatures, disubstituted carbamides are obtained; these, being insoluble in water, are easily separated from the mono-derivatives, which are soluble in hot water.

p-*Nitrophenyl propyl ether* is a reddish oil which boils at 285—287° with slight decomposition; p-*aminophenyl propyl ether* is a very unstable, colourless oil, and forms a *hydrochloride* crystallising in needles and melting at 171°, a *platinichloride*, and a *picrate* which blackens at 162° and melts at 176°. p-*Propyloxyphenylcarbamide* crystallises in colourless leaflets melting at 147°, *di*-p-*propyloxyphenylcarbamide* in silky needles melting at 201°, and p-*propyloxyphenylthiocarbamide* in needles melting at 158°.

p-*Nitrophenyl allyl ether* is obtained in needles and melts at 36°; the corresponding *amino*-compound is a reddish-yellow oil which forms a colourless hydrochloride melting at 205°, a platinichloride, and a picrate crystallising in small, yellow needles which melt at 164°. p-*Allyloxyphenylcarbamide* crystallises in small needles and melts at 154°; *di*-p-*allyloxyphenylcarbamide* melts at 211°. p-*Allyloxyphenylthiocarbamide* crystallises in small needles and melts at 148°; the corresponding disubstituted *carbamide* is similar and melts at 161°. p-*Nitrophenyl amyl ether* is a reddish oil which boils at 309—310° with partial decomposition; p-*aminophenyl amyl ether* is a yellowish oil, and forms a *hydrochloride* melting at 236°, a microcrystalline *platinichloride*, and an *acetyl* derivative which crystallises in small, lustrous needles and melts at 97°; the monosubstituted *carbamide* melts at 133°, the disubstituted *carbamide* crystallises in silky needles melting at 170°, and the monosubstituted *thiocarbamide* crystallises in colourless leaflets and melts at 157°.

p-*Nitrophenyl benzyl ether* forms microscopic needles, melts at 108°, and, when reduced with iron filings and acetic acid, yields the corresponding *amino*-compound, which crystallises in colourless leaflets, melts at 56°, and forms a crystalline *hydrochloride* melting at 213°, a *platinichloride*, and a *picrate* melting and decomposing at 155°; p-*benzyloxyphenylcarbamide* crystallises in needles and melts at 174°.

p-*Aminophenyl* iso*butyl ether* is a colourless oil and forms a *hydrochloride* crystallising in long needles which melt at 209°, and a picrate melting at 155°; p-iso*butyloxyphenylcarbamide* crystallises in colourless prisms melting at 156°, and the corresponding *thiocarbamide* melts at 158°. R. H. P.

Derivatives of Hydroxyquinol Triethyl Ether [1 : 2 : 4-Triethoxybenzene]. By E. Brezina (*Monatsh.*, 1901, **22**, 346—356. Compare Abstr., 1889, 247).—1 : 2 : 4-Triethoxybenzene is prepared from triacetoxybenzene by heating with ethyl iodide and potassium hydroxide. The *mononitro*-derivative ($NO_2 = 5$) is very readily formed, even by the action of dilute nitric acid on the ether, and is best prepared by nitrating in acetic acid solution; it crystallises in yellow needles melting at 108—109°. On reduction of the nitro-compound, an amino-derivative is obtained, which is oxidised by ferric chloride to 2 : 5-diethoxyquinone. 5-*Bromo*-1 : 2 : 4-*triethoxybenzene*, $C_6H_2Br(OEt)_3$, prepared by brominating the ether, forms white crystals melting at 51—52°, and by nitric acid is converted into the nitro-derivative previously described. 3 : 5 : 6-*Tribromo*-1 : 2 : 4-

triethxoybenzene, prepared by the action of excess of bromine on the monobromo-compound at 100°, forms crystals melting at 72—73°. This substance is also obtained by the action of bromine on the mononitro-derivative at 100°, the nitro-group being replaced by bromine. Nitric acid does not replace bromine from the tribromo-compound.

K. J. P. O.

Diphenylene Oxide in Coal Tar and the derived Diphenol. By Gustav Kraemer and Rudolf Weissgerber (*Ber.*, 1901, **34**, 1662—1667).—When the fluorene fraction of coal tar is purified by fusion with potassium hydroxide (this vol., i, 521), the aqueous alkaline solution contains a considerable quantity of 2 : 2′-dihydroxydiphenyl, which separates as a rapidly solidifying oil, and can be purified by recrystallisation from toluene. Contrary to the statement of Hodgkinson and Matthews (Trans., 1882, **41**, 168), the diphenol is not formed by repeatedly fusing pure fluorene with potassium hydroxide; its formation indicates the presence in commercial fluorene of diphenylene oxide, since the latter is converted into the diphenol on fusion with alkali. The yield of 2 : 2′-dihydroxydiphenyl from the oxide is considerably increased by carrying out the fusion in presence of phenanthrene as solvent. The converse transformation of the diphenol into the oxide is readily effected by fusion with zinc chloride.

The *sulphonic acid* derived from diphenylene oxide forms beautiful crystals, and is not hydrolysed by passing steam through its solution in sulphuric acid, although resolved on heating with hydrochloric acid under pressure. Diphenylene oxide differs from coumarone and furfuran in yielding a colourless solution in concentrated sulphuric acid.

2 : 2′-Dihydroxydiphenyl crystallises from water in lustrous leaflets which contain the solvent, melt at 73—75°, and effloresce in a desiccator; it boils at 315° under 768 mm. pressure. The *diacetyl* derivative separates from xylene in large, transparent crystals, and melts at 95°.

W. A. D.

Production of *o*-Hydroxyphenylethyl Alcohol from Coumarone and Synthesis of Hydrocoumarone. By Richard Stoermer and Bruno Kahlert (*Ber.*, 1901, **34**, 1806—1811).—When coumarone is heated with alcoholic potash at 200°, decomposition occurs, and the product contains (1) a small amount of substance which can be extracted by ether from the alkaline solution, and probably contains an unsaturated hydrocarbon; (2) *o*-hydroxyphenylacetic acid melting at 145°; and (3) a portion insoluble in sodium hydrogen carbonate. The last portion contains *o-hydroxyphenylethyl alcohol*,

$$OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}OH,$$

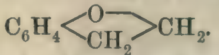
which is a thick, almost colourless oil without characteristic smell, boils at 168—169° under 12 mm. pressure, and has the sp. gr. 1·1531 at 18°, and the molecular refraction 38·5. The *sodium* salt is only sparingly soluble in aqueous soda. This compound and *o*-hydroxyphenylacetic acid are probably formed in the first instance by the simultaneous oxidation and reduction of hydroxyphenylacetaldehyde, produced by the splitting of the furfuran group of coumarone.

o-Hydroxyphenylethyl alcohol forms two compounds with phenylcyanate; the *monourethane*, $C_{15}H_{15}O_3N$, crystallises in white plates melting at 116—117°; the *diurethane*,

$$NHPh{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}NHPh,$$

crystallises in white needles melting at 130°.

o-Hydroxyphenylethyl alcohol is converted by hydrogen bromide into the *bromide*, $OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2Br$, an unstable oil which on treatment with aqueous soda yields hydrocoumarone,



$C_6H_4{<}\overset{O\text{—}}{\underset{CH_2}{}}{>}CH_2$.

o-Ethoxyphenylethyl alcohol boils at 136—137° under 14 mm. pressure, and is converted by oxidation into *o*-ethoxybenzoic acid. The urethane, $OEt{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}NHPh$, melts at 66°. A. H.

Action of Benzoyl Chloride on Ethyl Ether. By EDGAR WEDEKIND and J. HAEUSSERMANN (*Ber.*, 1901, **34**, 2081—2082).—Acid chlorides react with ether in the presence of anhydrous ferric chloride, ethyl chloride and the ethyl ester of the corresponding acid being produced. In most cases, the extent of the reaction is small, but in the case of benzoyl chloride as much as half of the chloride is converted into ethyl benzoate. A similar action of acetyl chloride in presence of zinc chloride has been observed by Descudé (this vol., i, 357). A. H.

Preparation of Simple and Compound Anhydrides. By A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 404—410).—One of the most convenient methods of preparing benzoic anhydride is by the addition of benzoyl chloride (1 mol.) to a solution of benzoic acid (1 mol.) in pyridine (1 mol.). When the reaction is finished, the product, after washing successively with warm water, dilute hydrochloric acid, sodium hydroxide solution, and warm water, and drying by means of fused sodium sulphate, is pure benzoic anhydride; pyridine hydrochloride is also formed in the reaction. Acetic anhydride is similarly obtained by the interaction of acetyl chloride, acetic acid, and pyridine. Also by the action of benzoyl chloride on a pyridine solution of acetic acid, the mixed acetic benzoic anhydride is formed; this compound readily undergoes decomposition, partly even in the cold, yielding acetic and benzoic anhydrides. T. H. P.

Conversion of Derivatives of Anthranilic Acid into Indigo. By HUGO ERDMANN (*J. pr. Chem.*, 1901, [ii], **63**, 385—391).—*Ethyl o-aminobenzoylformate*, $NH_2{\cdot}C_6H_4{\cdot}CO{\cdot}CO_2Et$, prepared by condensing ethyl formate and methyl *o*-aminobenzoate in the presence of sodium, forms colourless needles melting at 49°, which, on hydrolysis, yield only anthranilic acid. *Methyl methylene-o-aminobenzoate*,

$$CH_2{:}N{\cdot}C_6H_4{\cdot}CO_2Me,$$

obtained by the action of commercial formaldehyde on methyl *o*-aminobenzoate, crystallises in large, colourless crystals melting at 116·5°. With hydrogen bromide, it forms an unstable, yellow, additive *product* which melts and decomposes at 200°, and with bromine, a crystalline *dibromide* which, on heating at 175°, evolves carbon dioxide and yields a violet dye soluble in acids.

It is found that of all the derivatives of anthranilic acid, methyl *o*-cyanomethylacetaminobenzoate (see following abstract) yields indigo most easily, and in quantity. The ester is heated with naphthalene at 150—170°, and potassium hydroxide added; from the product pure indigotin can be extracted, representing 48 per cent. of the original ester.

K. J. P. O.

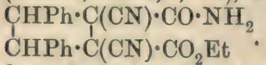
Action of Formaldehyde and Nascent Hydrogen Cyanide on Anthranilic Acid. By EMIL KOHNER (*J. pr. Chem.*, 1901, [ii], 63, 392—404. Compare preceding abstract).—*Anthranilidoacetonitrile* (*o-cyanomethylaminobenzoic acid*), $CN\cdot CH_2\cdot NH\cdot C_6H_4\cdot CO_2H$, prepared by the gradual addition of powdered potassium cyanide and formaldehyde to a solution of anthranilic acid in acetic acid, crystallises from alcohol in yellowish scales, melting and decomposing at 181°. The yield of pure nitrile amounts to 84 per cent. of the anthranilic acid employed. The solutions exhibit a violet fluorescence. The *sodium* salt, $C_9H_7O_2N_2Na,5H_2O$, forms yellowish prisms, the *silver* and *copper* salts anhydrous powders. Hydrolysis with potassium hydroxide converts the acid into phenylglycine-*o*-carboxylic acid. The *ethyl* ester, prepared by the action of ethyl iodide on the silver salt, forms colourless crystals melting at 89°. The *methyl* ester is readily obtained by the addition of a solution of methyl sulphate in methyl alcohol to a well stirred aqueous solution of the sodium salt at 40—50°, an alkaline reaction being maintained during the process by addition of aqueous sodium carbonate; the compound crystallises in yellowish needles melting at 106·5°. Although the acid cannot be acetylated, the methyl ester readily yields an *acetyl* derivative, $C_{12}H_{12}O_3N_2$, which forms crystals melting at 82—83°.

The nitroso-derivative, $C_9H_7O_3N_3$, of *o*-cyanomethylaminobenzoic acid, forms a yellowish powder melting at 113—114°; the *bromo*-derivative, $C_9H_7O_2N_2Br$, crystallises in colourless plates melting at 210—212°. The *bromo*-derivative of the methyl ester, $C_{10}H_9O_2N_2Br$, forms colourless crystals melting at 141—142°. K. J. P. O.

Condensation Products of Ethyl Cyanoacetate with Aldehydes. By CORRADO BERTINI (*Gazzetta*, 1901, 31, i, 265—279).—Compounds of the structure $CHR\colon C(CN)\cdot CO_2Et$, which are obtained by the condensation of aldehydes with ethyl cyanoacetate in presence of sodium ethoxide, should be capable of existing in two stereoisomeric modifications. By using piperidine as a condensing agent, the author finds that in some cases it is possible to obtain stereoisomerides of previously known compounds of this type.

The ethyl α-cyanocinnamate obtained from benzaldehyde and ethyl cyanoacetate in presence of sodium ethoxide is solid and melts at 51°. When piperidine is employed in place of the sodium ethoxide, however, a liquid *ethyl α-cyanocinnamate*, $C_{12}H_{11}O_2N$, is produced; it forms a faintly yellow oil insoluble in water and having a slight odour of bitter almonds; it is unchanged by long boiling in alcohol or benzene, but is mostly converted into the solid modification when distilled at the ordinary pressure; a total conversion is brought about by sodium ethoxide, or by very dilute solutions of sodium hydroxide or carbonate. Both forms of the ester have the normal molecular weight in boiling benzene, and both give the same compound when treated in the cold with alcoholic ammonia solution;

this compound, which has the melting point 168°, as was found by Carrick (Abstr., 1892, 1086), and not 187°, as was stated by Fiquet (Abstr., 1894, i, 32), the author considers to have the constitution



$$\begin{array}{l} CHPh\cdot C(CN)\cdot CO\cdot NH_2 \\ | \quad\quad\;\; | \\ CHPh\cdot C(CN)\cdot CO_2Et \end{array}$$

. By determining the volume of the water formed during the condensation of benzaldehyde and ethyl cyanoacetate, the author finds that the reaction takes place in two stages, the first resulting in the formation of an aldol which then loses, water: (1) $Ph\cdot CHO + CN\cdot CH_2\cdot CO_2Et = OH\cdot CHPh\cdot CH(CN)\cdot CO_2Et$; (2) $OH\cdot CHPh\cdot CH(CN)\cdot CO_2Et = H_2O + CHPh{:}C(CN)\cdot CO_2Et$.

Acetaldehyde also forms two stereoisomeric ethyl α-cyanocrotonates with ethyl cyanoacetate; with sodium ethoxide, liquid ethyl α-cyanocrotonate is obtained, whilst piperidine gives a viscous syrup, which shows a reddish-green fluorescence, and is probably ethyl α-cyano*iso*crotonate.

No stereoisomerides of the following substances could be obtained in this way. Ethyl α-cyano-β-*m*-nitrophenylacrylate, ethyl α-cyano-β-furylideneacrylate, ethyl methylenedioxyphenyl-α-cyanoacrylate, ethyl α-cyano-β-*p*-nitrophenylacrylate, ethyl α-cyano-β-*p*-methoxyphenylacrylate, ethyl α-cyanocinnamenylacrylate, or methyl α-cyanocinnamate.

T. H. P.

Triphenylacrylic Acid and Benzhydrol Ether. By HANS STOBBE and OTTO ZEITSCHEL (*Ber.*, 1901, **34**, 1963—1968).—When an ethereal solution of benzophenone and ethyl phenylacetate is treated with sodium ethoxide, some benzhydrol ether is formed; this gives a red solution with concentrated sulphuric acid, and when dissolved in a mixture of glacial acetic and sulphuric acids yields benzhydrol acetate. When benzophenone and benzyl cyanide are treated in a similar manner, a small quantity of triphenylacrylonitrile is formed; this dissolves in concentrated sulphuric acid, giving a violet solution.

R. H. P.

Glycerol Monosalicylate. By ERNST TÄUBER (*Ber.*, 1901, **34**, 1769—1770).—The insoluble oil produced by passing gaseous hydrogen chloride into a saturated solution of salicylic acid in glycerol at 100°, and described by Göttig (Abstr., 1878, 318) as glycerol monosalicylate, is in reality dichlorohydrin salicylate, $C_{10}H_{10}O_3Cl_2$ (compare Göttig, Abstr., 1891, 707). *Glycerol monosalicylate*, $OH\cdot C_6H_4\cdot CO_2\cdot C_3H_5(OH)_2$, is, however, produced when glycerol and salicylic acid are heated on a water-bath with a small amount of 60 per cent. sulphuric acid; it forms white, microscopic crystals, melts at 76°, is only slightly soluble in water, but very readily so in alcohol, and differs from the dichlorohydrin in that it is miscible with glycerol; it is readily hydrolysed by alkali hydroxides and carbonates.

T. M. L.

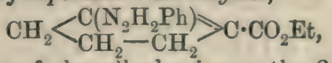
New Synthesis effected by the aid of Compounds containing the Methylene Group attached to one or two Acid Radicles: Action of Epichlorohydrin and Epibromohydrin on the Sodium Derivatives of Benzoylacetic Esters. By ALBIN HALLER (*Compt. rend.*, 1901, **132**, 1459—1463. Compare

Traube and Lehmann, Abstr., 1899, i, 417).—δ-Chloro-α-benzoyl-γ-valerolactone, $CHBz\text{<}\begin{matrix}CO\cdot O\\CH_2\end{matrix}\text{>}CH\cdot CH_2Cl$, is obtained by treating the sodium derivative of methyl or ethyl benzoylacetate (1 mol.) with epichlorohydrin (1 mol.) in absolute alcohol; it crystallises in needles and melts at 105—106°. The corresponding bromo-compound derived from epibromohydrin also crystallises in needles and melts at 92—93°. The *phenylhydrazone*, $C_{18}H_{16}O_2N_2Cl$, of the chloro-derivative melts at 148—150°. *δ-Benzoyl-αβ-butanediol*, $CH_2Bz\cdot CH_2\cdot CH(OH)\cdot CH\cdot OH$, results from the action of dilute potassium hydroxide solution on the chloro-lactone, the potassium salts of carbonic, benzoic, and dihydroxyvaleric acid being simultaneously produced; it melts at 90—91°, and its semicarbazone at 153—154°. G. T. M.

Cyclic β-Ketonecarboxylic Esters. By **Wilhelm Dieckmann** (*Annalen*, 1901, **317**, 27—109. Compare Abstr., 1899, i, 676, 914; 1900, i, 171, 297, 482, 623).—[In part with A. Groeneveld.]—In these experiments, made with the view of converting the esters of the succinic acid series into β-keto-monocarboxylates, the ethereal salt of the dibasic acid is treated with sodium in the presence of a small amount of absolute alcohol; the resulting *cyclo*ketonic acids are extracted either with alkalis or by conversion into their copper derivatives, or transformed into the corresponding cyclic ketone by the "ketone hydrolysis" by the action of mineral acids.

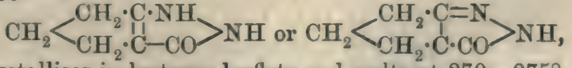
The ethyl esters of glutaric, azelaic, and sebacic acids do not yield well-defined products when subjected to this treatment. Ethyl suberate gives rise to an ester of the heptamethylene series which, although not isolated, is identified by conversion into suberone. Ethyl adipate yields ethyl 2-*cyclo*pentanonecarboxylate, which is transformed into *cyclo*pentanone when heated with dilute acid. The hydrolysis of the ester by cold dilute alkalis is a reaction of the first order, the velocity constant being independent of the concentrations of ethereal salt and alkali. The ester, when heated with excess of potassium methoxide in methyl alcohol, is hydrolysed to potassium adipate; with aqueous and alcoholic ammonia, it yields respectively adipamide and *ethyl* 2-*amino*-cyclo*pentene*-1-*carboxylate* melting at about 60°; the latter product is reconverted into the original ester by the action of dilute acids or ferric chloride, the change in the latter case being indicated by the development of a blue coloration.

2-*Phenylhydrazino*cyclo*pentene* 1-*carboxylate*,



$$CH_2\text{<}\begin{matrix}C(N_2H_2Ph)\\CH_2-CH_2\end{matrix}\text{>}C\cdot CO_2Et,$$

produced by the action of phenylhydrazine on the β-ketonic ester, melts at 93°, and neither forms a phenylpyrazolone nor develops a coloration with ferric chloride. Hydrazine hydrate, however, yields 3:4-cyclo*trimethylenepyrazolone*,

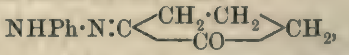


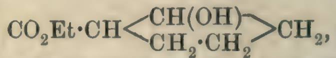
$$CH_2\text{<}\begin{matrix}CH_2\cdot C\cdot NH\\ \quad\ \|\\CH_2\cdot C-CO\end{matrix}\text{>}NH \text{ or } CH_2\text{<}\begin{matrix}CH_2\cdot C{=}N\\ \quad\ |\\CH_2\cdot C\cdot CO\end{matrix}\text{>}NH,$$

which crystallises in lustrous leaflets and melts at 270—275°.

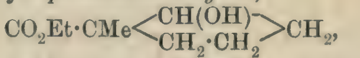
The *compound* $CO_2H\cdot[CH_2]_3\cdot CH(CO_2Et)\cdot CO\cdot NHPh$ arises from the interaction of phenylcarbimide and the β-ketonic ester; it melts at

148—150°. The *monoanilide*, $CO_2H\cdot[CH_2]_3\cdot CH(CO_2H)\cdot CO\cdot NHPh$ (m. p. 177°), results from the action of 2 mols. of an alkali hydroxide on the preceding compound, excess of the reagent gives rise to carboxyadipic acid, the monoanilide on heating, either alone or in water, loses carbon dioxide and yields the *monoanilide* of adipic acid, the product crystallises in white needles and melts at 152—153°.

The *monophenylhydrazone*,  $NHPh\cdot N{:}C<\begin{matrix}CH_2\cdot CH_2\\ CO\end{matrix}>CH_2$, of 1 : 2-diketo*cyclo*pentane, obtained by adding benzenediazonium chloride to a dilute acid solution of 2-*cyclo*pentanonecarboxylic acid, crystallises in reddish-yellow leaflets, melts at 203°, and yields the diphenylhydrazone on warming with an alcoholic solution of phenylhydrazine; these hydrazones give colour reactions with concentrated sulphuric acid and ferric chloride, the former yielding an indigo-blue and the latter a violet coloration.

Ethyl 2-cyclo*pentanolcarboxylate*,  $CO_2Et\cdot CH<\begin{matrix}CH(OH)\\ CH_2\cdot CH_2\end{matrix}>CH_2$, prepared by the action of 3 per cent. sodium amalgam on an alcoholic solution of the β-ketonic ester, is a colourless oil having a faint odour and boiling at 110—111° under 12 mm. pressure. The *acid* obtained from the ester by hydrolysis with cold potassium hydroxide and decomposition of the *potassium* salt is an uncrystallisable syrup yielding a sparingly soluble *silver* salt and readily losing water to form Δ^1-*cyclo*pentenecarboxylic acid.

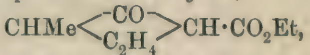
Ethyl 1-*methyl*-2-cyclo*pentanolcarboxylate*,



$$CO_2Et\cdot CMe<\begin{matrix}CH(OH)\\ CH_2\cdot CH_2\end{matrix}>CH_2,$$

resulting from the reduction of ethyl 1-methyl*cyclo*pentanonecarboxylate (compare Abstr., 1900, i, 171), is an oil boiling at 105—110° under 12—15 mm. pressure. The *acid* is uncrystallisable and boils at 160° under 12 mm. pressure; its potassium, zinc, copper, silver, calcium, and barium salts are described.

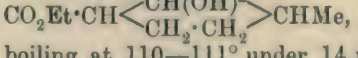
Ethyl 3-*methyl* 2-cyclo*pentanonecarboxylate*,



$$CHMe<\begin{matrix}CO\\ C_2H_4\end{matrix}>CH\cdot CO_2Et,$$

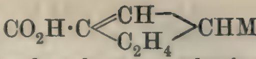
obtained by condensing ethyl α-methyladipate with sodium, boils at 108—109° or at 117—118° under 13 or 20 mm. pressure respectively, closely resembles ethyl 2-*cyclo*pentanonecarboxylate, giving a blue coloration with alcoholic ferric chloride, and a *copper* derivative melting at 166°; "ketone hydrolysis" leads to 3-methyl*cyclo*pentane, whilst "acid hydrolysis" furnishes α-methyladipic acid; its velocity constant of alkaline hydrolysis at 12·5° is 0·00144, whilst that of its non-methylated homologue is 0·00126.

Ethyl 3-*methyl* 2-cyclo*pentanolcarboxylate*,



$$CO_2Et\cdot CH<\begin{matrix}CH(OH)\\ CH_2\cdot CH_2\end{matrix}>CHMe,$$

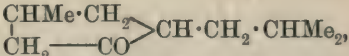
is a colourless oil boiling at 110—111° under 14 mm. pressure; the *acid* obtained by hydrolysing the ester with potassium methoxide boils at 160° under 12 mm. pressure. The *potassium* and *calcium* salts readily dissolve in water, whilst the silver salt is sparingly soluble.

3-*Methyl* Δ^1-cyclo*pentenecarboxylic acid*,  $CO_2H\cdot C{<}\begin{matrix}CH{-}\\C_2H_4\end{matrix}{>}CHMe$, obtained by distilling the preceding compound under atmospheric pressure, crystallises in colourless leaflets melting at 42°.

Ethyl 4-*methyl*-2-cyclo*pentanonecarboxylate*, produced by the condensation of ethyl β-methyladipate, is an oil boiling at 107—108° under 11—12 mm. pressure; its hydrolysis velocity constant at 12·5° is 0·00135. The *copper* derivative melts at 190°. The ester on "ketone hydrolysis" yields 3-methyl*cyclo*pentanone, "acid hydrolysis" furnishes β-methyladipic acid, whilst aqueous ammonia gives rise to β-methyladipamide, and a substance melting at 129° which is probably the amide of 4-methyl-2-*cyclo*pentanonecarboxylic acid; ethyl 2-amino-4-methyl*cyclo*pentenecarboxylate results from the action of alcoholic ammonia.

β-Methyl α-iso*butyladipic acid*, obtained by hydrolysing with baryta water the esters obtained by heating a mixture of ethyl 4-methyl-2-*cyclo*pentanonecarboxylate and *iso*butyl iodide with alcoholic sodium ethoxide, and distilling the less soluble portion of the product under diminished pressure, is an uncrystallisable syrup boiling at 235—237° under 30 mm. pressure.

4-*Methyl*-2-iso*butyl*cyclo*pentanone*,



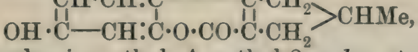
$\begin{matrix}CHMe\cdot CH_2\\ CH_2\text{——}CO\end{matrix}{>}CH\cdot CH_2\cdot CHMe_2$,

produced by treating an ethereal solution of the preceding ester with calcium oxide, boils at 196—197°; it has a faint odour of peppermint, and is optically active, having $[\alpha]_D$ 62°. The *oxime* crystallises in needles and melts at 92°, the *semicarbazone* melts at 163—164°.

Ethyl 4-*methyl*-1-iso*propyl*-2-cyclo*pentanonecarboxylate*, obtained by the action of *iso*propyl iodide on the sodium potassium derivative of ethyl 4-methyl-2-*cyclo*pentanonecarboxylate dissolved in xylene, is a colourless oil boiling at 130—131° under 15 mm. pressure.

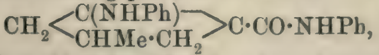
3-*Methyl* 1-iso*propyl*cyclo*pentanone*, formed by boiling the preceding ester with barium hydroxide solution, is an oil having an odour of menthone, and boiling at 180°; the *semicarbazone* melts at 182°.

Methyl αβ-cyclo*trimethyleneumbelliferone*,



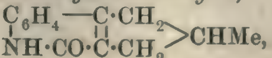
$$\begin{matrix}CH\cdot CH{:}C\text{———}C\cdot CH_2\\ OH\cdot C\text{—}CH{:}C\cdot O\cdot CO\cdot C\cdot CH_2\end{matrix}{>}CHMe,$$

produced by condensing ethyl 4-methyl-2-*cyclo*pentanonecarboxylate with resorcinol in the presence of concentrated sulphuric acid, crystallises with $1H_2O$, and melts at 110—120°; when anhydrous, it melts at 180°. Methyl *αβ-cyclo*trimethylenedaphnetin is obtained in a similar manner from pyrogallol; it crystallises with $1H_2O$ and melts at 120°; when anhydrous, the melting point is 207—210°. The *anilide*,



$$CH_2{<}\begin{matrix}C(NHPh)\text{—}\\CHMe\cdot CH_2\end{matrix}{>}C\cdot CO\cdot NHPh,$$

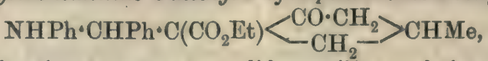
prepared by heating ethyl 4-methyl-2-*cyclo*pentanonecarboxylate with aniline at 150°, crystallises from alcohol in colourless, lustrous prisms and melts at 133°; when treated with concentrated sulphuric acid, it yields 3 : 4-*methyl*cyclo*trimethylenecarbostyril*,



$$\begin{matrix}C_6H_4\text{—}C\cdot CH_2\\NH\cdot CO\cdot C\cdot CH_2\end{matrix}{>}CHMe,$$

which melts at 253°, and gives rise to a *hydrochloride* crystallising in lustrous needles.

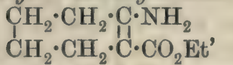
Ethyl benzylideneaniline 4-*methyl*-2-cyclo*pentanonecarboxylate*,

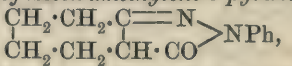


$$\mathrm{NHPh{\cdot}CHPh{\cdot}C(CO_2Et)}<\begin{matrix}\mathrm{CO{\cdot}CH_2}\\ \mathrm{CH_2}\end{matrix}>\mathrm{CHMe},$$

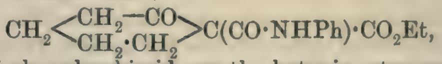
prepared by heating together benzylideneaniline and the corresponding ketone ester, melts at 108—110°.

Ethyl 2-*cyclo*hexanonecarboxylate, produced by the condensation of ethyl pimelate, has a hydrolysis velocity constant 20 times as great as that of the corresponding 2-*cyclo*pentanonecarboxylate; its copper derivative melts at 178°. The ester resembles the corresponding member of the pentamethylene series in its behaviour towards hydrolytic agents; dilute sulphuric acid gives rise to *cyclo*hexanone, dilute sodium hydroxide solution liberates the somewhat unstable ketonic acid, whilst excess of potassium hydroxide in methyl alcohol regenerates pimelic acid.

Ethyl Δ^1-*tetrahydroanthranilate* (*ethyl* 2-*amino*cyclo-Δ^1-*hexenecarboxylate*),  $\begin{matrix}\mathrm{CH_2{\cdot}CH_2{\cdot}C{\cdot}NH_2}\\ \mathrm{CH_2{\cdot}CH_2{\cdot}C{\cdot}CO_2Et}\end{matrix}$, is the principal product of the action of aqueous or alcoholic ammonia on ethyl-2-*cyclo*hexanonecarboxylate; it crystallises in nacreous leaflets and melts at 74°.

1-*Phenyl*-3 : 4-cyclo*tetramethylene*-5-*pyrazolone* [3-*keto*-2-*phenylhexahydroindazole*],  $\begin{matrix}\mathrm{CH_2{\cdot}CH_2{\cdot}C{=}N}\\ \mathrm{CH_2{\cdot}CH_2{\cdot}CH{\cdot}CO}\end{matrix}>\mathrm{NPh}$, is produced by mixing together the *cyclo*hexane ester and phenylhydrazine either alone or in ethereal solution; it melts at 165°.

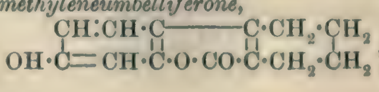
3 : 4-cyclo*Tetramethylene*-5-*pyrazolone* [2-*ketohexahydroindazole*] results from the action of hydrazine hydrate on the ketonic ester in alcoholic solution; it melts at 285—286°.

The *compound*,  $\mathrm{CH_2}<\begin{matrix}\mathrm{CH_2{-}CO}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}>\mathrm{C(CO{\cdot}NHPh){\cdot}CO_2Et}$, formed by the interaction of phenylcarbimide on the ketonic ester, melts at 108°; when heated with a methyl alcohol solution of potassium hydroxide, the ring opens, and the *acid* $\mathrm{CO_2H{\cdot}[CH_2]_4{\cdot}CH(CO_2H){\cdot}CO{\cdot}NHPh}$ is produced; this substance melts at 165°, and when heated above this temperature yields the *monoanilide* of pimelic acid (m. p. 113—114°).

Ethyl 1-*methyl*-2-cyclo*hexanonecarboxylate*, obtained by methylating the ketonic ester, is an oil boiling at 108—109° under 11—12 mm. pressure; the free acid is somewhat unstable, readily evolving carbon dioxide and becoming converted into 1-methyl*cyclo*hexanone. The *phenylhydrazone* of the preceding compound melts at 82°, and when boiled with glacial acetic acid it yields 1-*phenyl*-4-*methyl*-3 : 4-cyclo*tetramethylene*-5-*pyrazolone* [3-*keto*-2-*phenyl*-4-*methylhexahydroindazole*] melting at 138°.

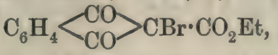
Ethyl 1-methyl-2-*cyclo*pentanonecarboxylate, when hydrolysed with potassium hydroxide dissolved in methyl alcohol, yields α-methylpimelic acid; ethyl α-methylpimelate is obtained by the action of sodium ethoxide.

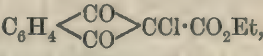
1 : 2-cyclo*Tetramethyleneumbelliferone*,

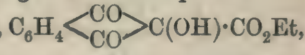


$$\begin{matrix}\mathrm{CH{:}CH{\cdot}C{-\!-\!-}C{\cdot}CH_2{\cdot}CH_2}\\ \mathrm{OH{\cdot}C{=}CH{\cdot}C{\cdot}O{\cdot}CO{\cdot}C{\cdot}CH_2{\cdot}CH_2}\end{matrix},$$

readily prepared by condensing ethyl 2-*cyclo*hexanonecarboxylate and resorcinol in the presence of concentrated sulphuric acid, is sparingly soluble in the organic solvents, yielding fluorescent solutions; it melts at 203—204°. G. T. M.

Action of Bromine and Chlorine on the Esters of Sodiodiketohydrindenecarboxylic Acid. By L. Flatow (*Ber.*, 1901, 2145—2149. Compare Abstr., 1900, i, 667).—*Ethyl bromodiketohydrindenecarboxylate*,  $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>CBr\cdot CO_2Et$, prepared by the action of the calculated quantity of bromine on ethyl sodiodiketohydrindenecarboxylate, suspended in carbon disulphide, forms crystals melting at 72—75°, which decompose in a few days at the ordinary temperature, and suddenly, at 80°, into carbon dioxide and bromodiketohydrindene. By the action of sodium hydroxide, the bromine is replaced by sodium, re-forming the original sodium compound; bromoform is produced at the same time. With potassium iodide, ethyl potassiodiketohydrindenecarboxylate is formed, with the separation of iodine. Bromodiketohydrindene is obtained when ethyl bromodiketohydrindenecarboxylate is boiled in absolute alcohol containing the calculated quantity of water, until the evolution of carbon dioxide ceases (compare Roser and Haselhoff, Abstr., 1888, 1304). Dibromodiketohydrindene is produced from the last-mentioned substance by heating with water until the solution becomes turbid. If the heating is prolonged, trisdiketohydrindene is formed. This compound was also synthesised by the action of sodium ethoxide on a mixture of dibromodiketohydrindene and diketohydrindene, thus confirming the constitution already assigned to it (*loc. cit.*).

Ethyl chlorodiketohydrindenecarboxylate,  $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>CCl\cdot CO_2Et$, prepared by the action of chlorine on an aqueous solution of the sodium compound, crystallises in long, colourless needles melting at 72—74°, and is far more stable than the corresponding bromine compound.

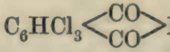
Ethyl hydroxydiketohydrindenecarboxylate,  $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C(OH)\cdot CO_2Et$, prepared by the action of sodium hydroxide on the chlorine compound, crystallises in needles melting at 120°, dissolves readily in alkalis with a yellow colour, and gives a violet colour with ferric chloride.

K. J. P. O.

3 : 4 : 6-Trichlorophthalic Acid. By Carl Graebe and S. Rostowzew (*Ber.*, 1901, **34**, 2107—2113. Compare Abstr., 1900, i, 546).—3 : 4 : 6-Trichlorophthalic acid is produced in the manufacture of dichlorophthalic acid, and is separated from the latter by converting the mixed acids into their acid ethyl esters, hydrolysing these compounds into their barium salts, and extracting the latter with hot water, until the final residue corresponds in composition with the formula $C_8HCl_3O_4Ba,H_2O$. The pure trichloro-acid separates from water in prismatic crystals, and is readily soluble in the ordinary organic solvents; at 150—160°, it is completely dehydrated, yielding the anhydride. This compound melts at 148°, sublimes in needles, and, when heated for 2 hours with methyl and ethyl alcohol, yields the corresponding esters; these substances solidify very slowly, and each consists, probably, of a mixture of two esters; the crystals separating from the methylated product melt at 84—86°, whilst the solid ethyl derivative melts at 89—105°.

The normal ethyl *ester*, $C_6HCl_3(CO_2Et)_2$, obtained from silver trichlorophthalate, is an oil which does not solidify at $-18°$.

Dichlorophthalic acid, when boiled for 2 hours with absolute alcohol, yields a mixture of acid and normal esters containing 1·6 per cent. of the latter.

3 : 4 : 6-*Trichlorophthalimide*,  $C_6HCl_3{<}\substack{CO\\CO}{>}NH$, prepared by dissolving the trichloro-acid or its anhydride in concentrated ammonia, crystallises from alcohol in needles melting at 236°; the acid is readily regenerated by the action of alkali hydroxides.

3 : 5 : 6-*Trichloroanthranilic acid* ($NH_2 = 2$), is readily obtained when the preceding compound is dissolved in water by the aid of 1 mol. of sodium hydroxide, and treated, first with sodium hypochlorite solution (active $Cl = 5·3$ per cent.), and then with sodium hydroxide; it crystallises from water and melts at 180°, being therefore isomeric with Beilstein and Kuhlberg's trichloroanthranilic acid (m. p. 210°). When heated at 180°, this trichloro-compound decomposes completely into 2 : 4 : 5-trichloroaniline. This result indicates the constitutions of the trichlorophthalic acid, and the trichloroanthranilic acid derived from it.

o-*Trichlorobenzoylbenzoic acid* ($Cl_3 = 3 : 4 : 6$ or $3 : 5 : 6$), results from the condensation of 3 : 4 : 6-trichlorophthalic anhydride with benzene in the presence of aluminium chloride; it separates from chloroform in colourless crystals and melts at 177°. This acid dissolves in the ordinary organic solvents and in solutions of the alkali carbonates; it is, however, only sparingly soluble in water.

1 : 2 : 4-*Trichloroanthraquinone*, produced by heating the preceding compound with concentrated sulphuric acid, forms yellow crystals and melts at 185°; it readily dissolves in benzene or chloroform, but is only sparingly soluble in ether, acetic acid, or alcohol. When fused with alkali hydroxides, the quinone yields phthalic acid.

G. T. M.

isoPropylphthalide. By PIETRO GUCCI (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 473—476).—The view that the oily product boiling at 225—229° under 160 mm. pressure, obtained by the action of zinc dust on *iso*propyl iodide and phthalic anhydride (Abstr., 1899, i, 513), is *iso*propylphthalide, is confirmed by an examination of the compounds it yields with sodium hydroxide, which are found to be sodium benzoate and *iso*butyrate. The identity of the compound with Roser's *iso*propylphthalide (Abstr., 1885, 268) is also established, and hence the correctness of the constitution assigned to the latter product.

T. H. P.

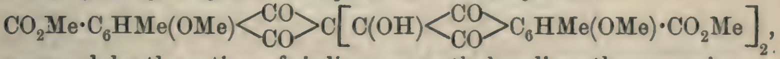
Benzylated Ethyl Acetonedicarboxylates. By FRITZ FICHTER and HEINRICH SCHIESS (*Ber.*, 1901, 34, 1996—2001).—The product of the action of sodium ethoxide on benzyl chloride and ethyl acetonedicarboxylate contains the esters of mono-, di-, and tri-benzylacetonedicarboxylic acids; the *tribenzyl* derivative, $C_{30}H_{32}O_5$, was isolated in glistening needles melting at 82°, and is perhaps identical with the substance melting at 92° which von Pechmann and Dünschmann (Abstr., 1891, 674) described as a dibenzyl derivative. When hydrolysed with alkalis, it gives benzylmalonic acid, and dibenzylacetic acid and its *ethyl* ester; the latter, $C_{18}H_{20}O_2$, crystallises from dilute alcohol in large prisms and melts at 88—89°.

By reducing with aluminium amalgam a crude mixture of esters containing the monobenzyl ester, *β-hydroxybenzylglutaric acid*, $C_{12}H_{14}O_5$, has been prepared; it crystallises from a mixture of ether and light petroleum, melts at 126—128°, and gives a crystalline *barium* salt.

T. M. L.

Carminone Compounds. By Carl Liebermann and Josef Landau (*Ber.*, 1901, **34**, 2153—2163. Compare Abstr., 1900, i, 661).—The name "carminone" is suggested for 5-hydroxy-7-methyldiketohydrindene, and "carminonecarboxylic acid" for 5-hydroxy-7-methyldiketohydrindene-4-carboxylic acid. It is found that the tetramethyl derivative of cochinelic acid is best prepared by heating the acid (1 mol.) with silver oxide (3—4 mols.) and excess of methyl iodide at 100° (compare *loc. cit.*).

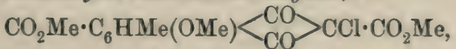
Methyl dihydroxytris-methoxycarminonecarboxylate,



$$\mathrm{CO_2Me\cdot C_6HMe(OMe)}<\begin{matrix}\mathrm{CO}\\\mathrm{CO}\end{matrix}>\mathrm{C}\left[\mathrm{C(OH)}<\begin{matrix}\mathrm{CO}\\\mathrm{CO}\end{matrix}>\mathrm{C_6HMe(OMe)\cdot CO_2Me}\right]_2,$$

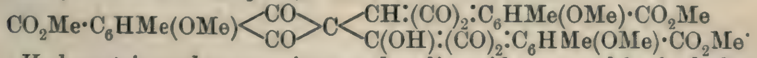
prepared by the action of iodine on methyl sodiomethoxycarminonedicarboxylate, forms a white powder decomposing at 175°, and dissolves in alkalis with a yellow colour which rapidly becomes deep red in the air. From the red solution, acids throw down a red precipitate (compare this vol., i, 552).

Methyl chloromethoxycarminonedicarboxylate,



$$\mathrm{CO_2Me\cdot C_6HMe(OMe)}<\begin{matrix}\mathrm{CO}\\\mathrm{CO}\end{matrix}>\mathrm{CCl\cdot CO_2Me},$$

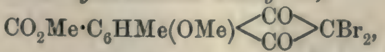
prepared by the action of chlorine on the sodium derivative, crystallises in colourless needles melting at 165—166°, and decomposes when boiled with water with elimination of hydrogen chloride. The corresponding *bromine* derivative forms needles melting at 168—170°, and is far less stable than the chlorine compound. With sodium iodide, it yields the sodium compound just mentioned. When boiled with aqueous methyl alcohol, the bromine derivative is converted into a *compound* decomposing at 275—276°, which is probably *methyl hydroxytris-methoxycarminonecarboxylate*,



$$\mathrm{CO_2Me\cdot C_6HMe(OMe)}<\begin{matrix}\mathrm{CO}\\\mathrm{CO}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{CH{:}(CO)_2{:}C_6HMe(OMe)\cdot CO_2Me}\\\mathrm{C(OH){:}(CO)_2{:}C_6HMe(OMe)\cdot CO_2Me}\end{matrix}.$$

Hydroxytris-methoxycarminonecarboxylic acid, prepared by hydrolysing the last-mentioned substance with potassium hydroxide, exists in a deep red and a pale yellow modification. Acetone converts the former into the latter, and alkalis induce the reverse change.

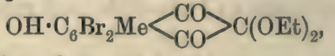
Methyl dibromomethoxycarminonecarboxylate,



$$\mathrm{CO_2Me\cdot C_6HMe(OMe)}<\begin{matrix}\mathrm{CO}\\\mathrm{CO}\end{matrix}>\mathrm{CBr_2},$$

prepared by brominating methyl bromomethoxydicarboxylate, crystallises in colourless needles melting at 141—143°, which liberate iodine from sodium iodide, and lose both bromine atoms when treated with aqueous methyl alcohol or silver oxide; the two bromine atoms are therefore not in the benzene nucleus.

α-Bromocarmin (2 : 2 : 4 : 6-tetrabromocarminone), when boiled with aqueous sodium carbonate, yields bromoform, dibromohydroxyhomophthalic acid, and a colouring matter which exists in a red and a colourless form; the latter is converted into the former by alkalis. The composition of this substance could not be fixed, but it has lost two of the four bromine atoms present in α-bromocarmin.

Dibromodiethoxycarminone,  $OH\cdot C_6Br_2Me<\!\begin{smallmatrix}CO\\CO\end{smallmatrix}\!>C(OEt)_2$, prepared from α-bromocarmin by the action of alcohol in the presence of silver oxide, crystallises in yellow needles melting at 182—184°, and dissolving in alkalis with a yellow colour. K. J. P. O.

Secondary Products of the Action of Sulphuric Acid on Wood Charcoal. By AUGUSTE VERNEUIL (*Compt. rend.*, 1901, **132**, 1340—1343. Compare Abstr., 1894, i, 217).—Benzenepentacarboxylic acid, separated by fractional precipitation with barium hydroxide from the product of the action of sulphuric acid on wood charcoal, exhibits a distinct, greenish-yellow phosphorescence lasting about 6 seconds. This effect is due to an impurity, for the colourless crystals of the compound obtained from its purified lead salt by decomposition with hydrogen sulphide are devoid of this property. These crystals do not contain $6H_2O$, as formerly supposed, but have the composition $C_6H(CO_2H)_5,5H_2O$; they crystallise in the rhombic system, and have a very well marked double refraction and high dispersive power.

Pyromellitic acid has also been isolated from the products of the action of sulphuric acid on wood charcoal, the yield amounting to 2 per cent. It crystallises from water with 2 mols. of the solvent, and is readily separated from benzenepentacarboxylic acid on account of its slight solubility. Besides mellitic acid, no other crystalline compounds have been isolated from the products of this action. The charcoal employed had the following composition, C, 87·62; H, 2·55; O, 8·38; ash, 1·43, the excess of hydrogen over the amount required by the oxygen to form water being 1·51.

There is undoubtedly some connection between the presence of the hydrogen and the formation of the benzenoid acids, for this wood charcoal, after being calcined at a bright red heat, is only very slowly attacked by sulphuric acid, and does not yield mellitic or benzenepentacarboxylic acid. G. T. M.

Compounds from Lichens. By WILHELM ZOPF (*Annalen*, 1901, **317**, 110—145. Compare Abstr., 1895, i, 297; 1896, i, 103; 1897, i, 255, 362, 436; 1898, i, 89, 489; 1899, i, 716).—*Placodium alphophacum* contains salazinic acid but not psoromic acid as previously suggested. *P. crassum* contains a relatively large amount of usnic acid, and a very small quantity of psoromic acid; this is invariably true, whatever be the habitat of the lichen.

The crystalline yellowish-green and colourless acids derived from *P. gypsaceum* and *P. Lagascæ* are usnic and psoromic acid respectively, the latter being identified by conversion into parellinic acid (m. p. 230°), by heating with aqueous sodium hydroxide solution.

The thallus of *P. fulgens* yields parietin and a colourless substance which is neither usnic nor psoromic acid.

Pachnolepia decussata, when extracted with ether, yields a mixture of crystalline substances containing atranoric and lecanoric acids, and a small amount of a compound crystallising in prisms insoluble in potassium hydroxide solution, and not reddened by calcium hypochlorite.

Sticta aurata, whether grown in France or in the Transvaal, yields about 5·5—6 per cent. of stictaurin; this substance forms the yellow colouring matter of *S. flavicans*, *S. crocata*, *S. impressa*, and *S. orygmæa.* The last-named lichen contains, in addition, a new acid, *orygmæanic acid*, crystallising in brown, monoclinic plates or prisms and melting at 310°. The solutions of this acid in organic solvents have a red colour; in alkaline solutions it dissolves, giving a violet coloration; its *sodium*, *calcium*, and *barium* salts are described.

Parmelia locarnensis yields gyrophoric acid and a new substance, *imbricaric acid*, melting at 103—104°; in melting point, this acid resembles rangiformic and atranoric acids, differing from the former, however, in developing a violet coloration with ferric chloride, and from the latter in being precipitated from its ethereal solution on the addition of potassium carbonate.

Diffusin, which was formerly obtained from *Parmelia diffusa*, also exists in *P. sorediata*; the two specimens agree in all respects, and are totally different from lecanoric acid, also stated by Hesse to exist in *P. sorediata.*

Lobaric acid, derived from *Parmelia omphalodes*, melts at 192—193°, has the composition $C_{24}H_{26}O_8$, and is identical with the author's stereocaulic acid (Abstr., 1896, i, 103) and Hesse's usnetic acid; it has already been extracted from nine species of lichens.

Divaricatic and usnic acids are always found together in specimens of *Evernia divaricata* grown in different localities.

Umbilicaric acid, found in *Gyrophora polyphylla*, is accompanied by gyrophoric acid.

Alectoria cana develops an intense yellow coloration with sodium hydroxide solution, which is not given by the allied species, *A. implexa*; the former lichen yields salazinic acid, whilst the latter does not. Hesse, who had probably confounded these two species, states that *A. cana* contains alectoric acid, but no salazinic acid.

The yellow colouring matter in the rare *Pertusaria lutescens* is probably thiophaninic acid, $C_{12}H_6O_9$, obtained from thiophanic acid by Hesse by the action of hydrogen iodide.

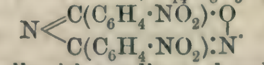
Mallotium Hildenbrandii has not hitherto yielded any lichen acids, but only a small quantity of a crystalline substance of the phytosterol type. G. T. M.

Chemical Action of Light. II. By Giacomo L. Ciamician and Paul G. Silber (*Ber.*, 1901, **34**, 2040—2046. Compare this vol., i, 329).—When *o*-nitrobenzaldehyde is exposed to light, either in solution in benzene, ether, or acetone, or as a thin, crystalline layer obtained by moistening the inside of a flask with its benzene solution and allowing the solvent to evaporate, it is converted into *o*-nitrosobenzoic acid. In methyl alcoholic solution, *methyl* o-*nitrosobenzoate* is obtained, separating in colourless, rhombic plates melting at 152—153° to an emerald green liquid. *Ethyl* o-*nitrosobenzoate*, obtained by the action of light on an alcoholic solution of *o*-nitrobenzaldehyde, is deposited in well-formed, colourless crystals melting at 120—121° to an emerald green liquid. In *iso*propyl alcoholic solution, the action of light on *o*-nitrobenzaldehyde yields *o*-nitrosobenzoic acid, whilst in paraldehyde solution, together with this acid, a small quantity of a neutral *compound*, $C_9H_7O_3N$, is formed, which gives colourless solutions and separates from alcohol in large, colourless prisms melting at 121° to a colourless liquid ; it reduces ammoniacal silver solution and does not give an indigo-blue coloration when boiled with alkali.

The action of light on solutions of *m*- and *p*-nitrobenzaldehyde gave no definite products. T. H. P.

Oxidation of Aromatic and Aliphatic Aldoximes. By EUGEN BAMBERGER and THOR SCHEUTZ [in part with R. SELIGMANN] (*Ber.*, 1901, **34**, 2023—2033).—Benzonitrile is found amongst the products of oxidation of benzaldoxime by permonosulphuric acid (Caro's reagent ; Abstr., 1900, i, 500). Under similar conditions, anisaldoxime gives anisaldehyde, anisic acid, anisonitrile, anishydroxamic acid, and anisylnitromethane. *Anisylnitromethane*, $OMe\cdot C_6H_4\cdot CH_2\cdot NO_2$, is a pale yellowish oil, which readily distils in a current of steam, and dissolves completely when shaken with alkali hydroxides ; it shows Konowaloff's reaction, and its alkaline solution deposits a violet-brown *ferric* salt when mixed with ferric chloride. *Anisylnitroformaldehydephenylhydrazone*, $OMe\cdot C_6H_4\cdot C(NO_2):N_2HPh$, prepared by the action of phenyldiazonium acetate on the preceding compound, crystallises from alcohol in glistening, red needles, melts with liberation of gas at 114° (corr.) ; it dissolves in dilute alkali hydroxides, but concentrated sodium hydroxide precipitates the *sodium* salt in needles with a bronze-like lustre.

m-Nitrobenzaldoxime gives *m*-nitrobenzhydroxamic acid, *m*-nitrobenzoic acid, and a substance, $C_{14}H_8O_5N_4$, which is probably *dinitrodibenzenylazoxime*,



$$N\left\langle\begin{array}{l}C(C_6H_4\cdot NO_2)\cdot O\\ C(C_6H_4\cdot NO_2):N\end{array}\right.$$

The latter crystallises from alcohol in pale yellowish needles and melts at 147·5—149·5° ; *m*-nitrobenzamide, *m*-nitrobenzonitrile, and *m*-nitrophenylnitromethane could not be detected.

p-Nitrobenzaldoxime gives *p*-nitrobenzhydroxamic acid, but the oxidation has not been further studied.

Acetaldoxime gives chiefly acetic acid, but acethydroxamic acid, nitroethane, and acetonitrile are also produced.

Propaldoxime gives prophydroxamic acid and a small amount of nitropropane.

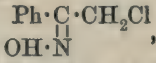
Valeraldoxime gives valerhydroxamic acid and a small amount of nitropentane ; *valerhydroxamic acid*, $CHMe_2\cdot CH_2\cdot C(OH):NOH$, melts at 73·5—76°, crystallises in white, pearly flakes or flat needles, and, unlike most hydroxamic acids, is readily soluble in ether.

*iso*Butyraldoxime gives *iso*butyrhydroxamic acid and nitrobutane.

T. M. L.

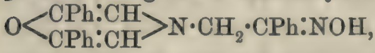
Action of Sodium Ethoxide on Mixtures of Ketones and Ethyl Malonate. By HANS STOBBE [and in part GEORG HEUN] (*Ber.*, 1901, 34, 1955—1962).—When a mixture of acetone and ethyl malonate is treated with sodium ethoxide suspended in ether, the principal products obtained are ethyl dimethyldihydroresorcylate and dimethyldihydroresorcinol. Benzophenone, when treated in a similar manner, yields diphenylcarbinol; acetophenone yields benzoic acid, a *compound*, $C_{24}H_{18}O$, which melts at 183°, phenylmethylcarbinol, and a *hydrocarbon*, $C_{16}H_{14}$, which crystallises in large plates or prisms, and melts at 131—132°. In these cases, the sodium ethoxide appears to have acted as a reducing agent. R. H. P.

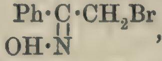
ω-Halogenacetophenone Oximes. By H. KORTEN and ROLAND SCHOLL (*Ber.*, 1901, 34, 1901—1910).—The view which has been several times put forward that α-halogen ketones containing the grouping ·CO·CHCl are converted by hydroxylamine directly into glyoximes without the formation of intermediate products was shown by Scholl and Mathaiopoulos (Abstr., 1896, i, 520) to be erroneous in the case of aliphatic compounds which under suitable conditions yield α-halogenketoximes. The authors find that analogous compounds can be obtained in the aromatic series if the hydroxylamine be made to act in presence of a mineral acid. In this way, ω-halogenacetophenones yield aromatic α-halogenketoximes, which are readily crystallisable compounds belonging to the *syn*-phenyl series. When the hydroxylamine is employed in alkaline solution, the glyoxime obtained is accompanied by a small proportion of the *anti*-phenyl ketoxime. The halogen of these α-halogenketoximes readily reacts with alkalis and ammonia, the latter yielding tertiary amines which, under the action of alcoholic hydrochloric acid, are partially de-oximated and transformed into paroxazine derivatives.

syn-*Phenylchloromethylketoxime*,  $\begin{array}{l}\mathrm{Ph\cdot C\cdot CH_2Cl}\\ \quad\ \ \|\\ \mathrm{OH\cdot N}\end{array}$, obtained by the interaction of ω-chloroacetophenone (1 mol.) and hydroxylamine hydrochloride (3 mols.) in aqueous methyl alcoholic solution at the ordinary temperature, separates from carbon disulphide in crystals melting at 88·5—89°. Its vapours are very painful to the eyes, whilst when placed on the skin in either the solid or dissolved state, it produces a very persistent burning sensation. When it is treated with phosphorus pentachloride in ethereal solution, and the product decomposed with water, chloroacetanilide is obtained. With phenylcarbimide, it yields *carbanilidosynphenylchloromethylketoxime*, $CH_2Cl\cdot CPh\colon N\cdot O\cdot CO\cdot NHPh$, crystallising from light petroleum in colourless needles melting at 118—120°, and with acetic anhydride, the *acetyl* derivative, $CH_2Cl\cdot CPh\colon N\cdot OAc$, separating from light petroleum in needles melting at 67—68°, is obtained. With concentrated ammonia solution in the cold, the oxime gives

Trihydroxyiminotriphenacylamine, $N(CH_2\cdot CPh{:}N\cdot OH)_3$, which forms shining leaflets melting and decomposing at 222°; it is readily soluble in sodium hydroxide solution, and is reprecipitated by dilute acids. With hot concentrated hydrochloric acid, it yields *two hydrochlorides*, (1) a colourless compound, $C_{24}H_{22}O_3N_2,2HCl,H_2O$, crystallising from acetic acid in shining, white leaflets melting at 242°; its solution in concentrated sulphuric acid becomes dark blue on heating, whilst on cooling and adding water it changes first to violet, then to rose red, and finally loses its colour, and gradually deposits colourless needles, possibly of a sulphate. The free *base*, probably

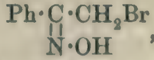
$$N(CH_2\cdot COPh)_2\cdot CH_2\cdot CPh{:}N\cdot OH,$$

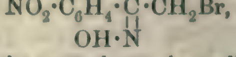
corresponding with this hydrochloride crystallises from dilute alcohol in yellowish needles melting at 92°. (2) A yellow salt, $C_{24}H_{20}O_2N_2,HCl$, separating from alcohol in small, yellow crystals melting and decomposing at 208°; it dissolves in the ordinary organic solvents except ether and light petroleum, and when heated with concentrated sulphuric acid gives a reddish-yellow solution. The free *base*, probably  $O<\begin{matrix}CPh{:}CH\\CPh{:}CH\end{matrix}>N\cdot CH_2\cdot CPh{:}NOH$, is deposited from dilute alcoholic solution in yellowish-red crystals melting at 191°; the dilute alcoholic solution exhibits a yellowish-red fluorescence, and dyes animal fibres a yellowish-red colour.

syn-*Phenylbromomethylketoxime*,  $\begin{matrix}Ph\cdot C\cdot CH_2Br\\ \| \\ OH\cdot N\end{matrix}$, obtained, together with a small proportion of the *anti*-compound as a mixture melting at 92°, when ω-bromoacetophenone (1 mol.) and hydroxylamine hydrochloride (3 mols.) react in aqueous methyl alcoholic solution at the ordinary temperature, separates from light petroleum in crystals melting at 89·5°; it dissolves readily in the ordinary organic solvents, and when placed on the skin, especially in solution, it causes a burning feeling, whilst its vapours vigorously attack the eyes. The oxime melting at 92°, when treated with phosphorus pentachloride in ethereal solution and afterwards with water, gives monobromoacetanilide. *Carbanilino*syn*phenylbromomethylketoxime*,

$$CH_2Br\cdot CPh{:}N\cdot O\cdot CO\cdot NHPh,$$

crystallises from a mixture of benzene and light petroleum in silky needles melting at 120—121°. *Acetyl*syn*phenylbromomethylketoxime*, $CH_2Br\cdot CHPh{:}N\cdot OAc$, melts at 74—75°. The action of ammonia on ω-bromoacetophenoneoxime yields the trihydroxyiminotriphenacylamine melting at 222°.

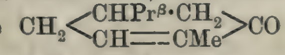
anti-*Phenylbromomethylketoxime*,  $\begin{matrix}Ph\cdot C\cdot CH_2Br\\ \| \\ N\cdot OH\end{matrix}$, when crystallised from light petroleum, melts at 96·5—97°; when kept, it decomposes and turns yellow.

syn-m-*Nitrophenylbromomethylketoxime*,  $\begin{matrix}NO_2\cdot C_6H_4\cdot C\cdot CH_2Br,\\ \| \\ OH\cdot N\end{matrix}$ crystallises from a mixture of benzene and light petroleum in yellowish needles melting at 126·5—127°; it has practically no action on the skin or eyes, and is much more stable than the non-nitrated derivative. When treated with phosphorus pentachloride in ethereal solution, and afterwards with water, it yields *m*-nitrobromoacetanilide. *Carbanilino*-m-*nitro-ω-bromoacetophenoneoxime*, $NO_2\cdot C_6H_4\cdot C(CH_2Br)\colon N\cdot O\cdot CO\cdot NHPh$, separates from a mixture of benzene and light petroleum in yellowish needles melting at 145—146°. *Acetyl*-m-*nitro-ω-bromoacetophenoneoxime*, $NO_2\cdot C_6H_4\cdot C(CH_2Br)\colon N\cdot OAc$, crystallises from a mixture of light petroleum and benzene in yellowish needles melting at 64—65°.

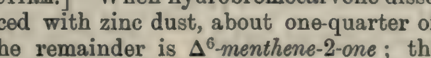
T. H. P.

Auto-oxidation of Carvone. By CARL D. HARRIES (*Ber.*, 1901, **34**, 2105—2106).—When carvone, barium hydroxide, and methyl alcohol are shaken for some considerable time in contact with oxygen, the ketone slowly dissolves, and the solution then contains barium peroxide and 1-methyl-4-propenyldihydroresorcinol formed in accordance with the following equation, $C_{10}H_{14}O + H_2O + O_2 = H_2O_2 + C_{10}H_{14}O_2$; this diketone is identical with the product obtained by oxidising hydroxylaminocarvoxime (compare Abstr., 1898, i, 568; 1899, i, 583). The diketone is accompanied by a small amount of a product having the odour of strawberries which has not been investigated.

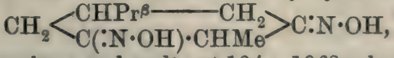
G. T. M.

Δ⁶-Menthene-2-one and Carvotanacetone. By CARL D. HARRIES (*Ber.*, 1901, **34**, 1924—1935).—Carvotanacetone is the racemic form of the ketone  $CH_2<\begin{matrix}CHPr^\beta\cdot CH_2\\ CH{=\!=}CMe\end{matrix}>CO$ (compare Semmler, Abstr., 1900, i, 676), and the dihydrocarvone now obtained by the reduction of hydrobromocarvone is its optically active modification.

[With CARL STIRM.]—When hydrobromocarvone dissolved in methyl-alcohol is reduced with zinc dust, about one-quarter of the product is carvone, and the remainder is Δ⁶-*menthene-2-one*; this is a bright yellow, strongly refractive oil, which boils at 227—228°, or at 96—97° under 9 mm. pressure, has a sp. gr. 0·9411 at 10° and 0·9351 at 19°, and in a 10 cm. tube at 25° has α_D +49·5°. The *semicarbazone* crystallises in plates, sinters at 170°, and melts at 173—174°; the *compound* with hydrogen sulphide, $2C_{10}H_{16}O,H_2S$, crystallises in lustrous needles and melts at 222—225°; the *oxime* crystallises in large prisms and melts at 75—77°. The *oxaminoxime*,



$$CH_2<\begin{matrix}CHPr^\beta\text{———————}CH_2\\ CH(NH\cdot OH)\cdot CHMe\end{matrix}>C\colon N\cdot OH,$$

obtained when the ketone remains for eight days with an alcoholic solution of hydroxylamine, crystallises with $\frac{1}{2}H_2O$ in felted needles, which sinter at 90° and melt at 95—97°, forms an *oxalate* melting at 130—135°, and when oxidised slowly by a current of air yields the *dioxime*,  $CH_2<\begin{matrix}CHPr^\beta\text{————}CH_2\\ C(\colon N\cdot OH)\cdot CHMe\end{matrix}>C\colon N\cdot OH$, which crystallises in colourless prisms and melts at 194—196°, when it decomposes. When reduced with zinc dust and an alcoholic solution of sodium hydroxide, the ketone yields *d*-carvomethone and when reduced with aluminium amalgam, a dimolecular *compound*, $C_6H_7MePr^\beta O\cdot C_6H_7MePr^\beta O$, which is a syrup, but yields a *phenylhydrazone* melting at 260°. The ketone slowly combines with hydrogen bromide, forming a yellow oil, which, when treated with lead nitrate, yields the original compound.

The semicarbazone obtained from Semmler's carvotanacetone (*loc. cit.*) melted at 177°, and the oxaminoxime sintered at 155° and melted at about 162°. This oxaminoxime could not be obtained quite pure, and it is probable that "carvotanacotone" is a mixture of the racemic form of the ketone (dihydrocarvone) with other compounds.

R. H. P.

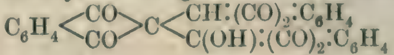
1 : 3 : 5-Triacylated Benzenehydrocarbon and some Compounds of Di-chloroacetylmesitylene. By FRANZ KUNCKELL and A. HILDEBRANDT (*Ber.*, 1901, **34**, 1826—1829).—When acetylmesitylene is treated with chloroacetyl chloride and aluminium chloride in sunlight, the two remaining hydrogen atoms of the nucleus are replaced by the chloroacetyl group and *di-chloroacetylmesitylene*,

$$C_6Me_3Ac(CO\cdot CH_2Cl)_2,$$

is produced, which forms white, compact crystals melting at 130°. It has not, however, been found possible to replace the three hydrogen atoms by either the acetyl or chloroacetyl group.

Dinitro-2 : 4 : 6-*trimethylbenzoic acid*, $C_6Me_3(NO_2)_2\cdot CO_2H$, formed by the action of nitric acid on di-chloroacetylmesitylene, crystallises in long, white needles melting at 230—231°. The *chloride* crystallises in white needles melting at 154—155°; the *anilide* crystallises in white needles melting at 300—310°; and the *phenylhydrazide* forms white needles melting above 300°. Di-chloroacetylmesitylene is converted by bromine into a crystalline compound melting at 162—163°, which has the formula $C_{13}H_9O_2Cl_2Br_5$, but the constitution of which has not yet been ascertained. When treated with phenylhydrazine in benzene solution, it yields *di-chloroacetylbromomesitylene*, which crystallises in white, lustrous plates melting at 113°.

A. H.

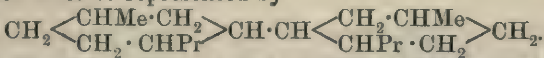
Hydroxytris-diketohydrindene. By CARL LIEBERMANN and JOSEF LANDAU (*Ber.*, 1901, **34**, 2149—2152. Compare Abstr., 1900, i, 667).—Hydroxytris-diketohydrindene, $C_{27}H_{14}O_7$, is formed when a solution of tris-diketohydrindene in potassium hydroxide is boiled with free access of air. The initially colourless solution becomes deep red; from this, acids precipitate the hydroxy-compound as a deep red powder melting and decomposing at 218—219°, and readily soluble in warm water or chloroform. By recrystallisation from acetic acid, it is transformed into a colourless or faintly yellow, isomeric acid, which crystallises in leaves melting and decomposing at 225—228°, insoluble in water or chloroform. The yellow modification is immediately transformed into the red by dissolving in alkalis, ammonia, or pyridine. The formula  $C_6H_4<\substack{CO\\CO}>C<\substack{CH:(CO)_2:C_6H_4\\C(OH):(CO)_2:C_6H_4}$ is suggested for one of the acids.

From the colourless solution of tris-diketohydrindene in potassium hydroxide, acids precipitate tris-diketohydrindene unchanged. On boiling a solution in some excess of alkali without access of air, red needles separate which proved to be *iso*ethinediphthalide (Gabriel and Leupold, Abstr., 1898, i, 481 and 482).

The golden-yellow potassium and the red barium salts, previously described (Abstr., 1900, i, 667), are shown to be derivatives of hydroxytris-diketohydrindene, and to have respectively the formulæ $C_{27}H_{12}O_7K_2$ and $C_{27}H_{12}O_7Ba$.

K. J. P. O.

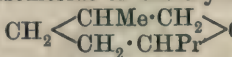
Haloid Derivatives of Menthol, and Hydrocarbons derived from them. By NICOLAI KURSANOFF (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 289—302).—When menthyl chloride, obtained by the action of phosphorus pentachloride on menthol in light petroleum solution, is dissolved in ether and the solution boiled with an excess of sodium, it gives rise to menthene, menthane, and two dimenthyls, $C_{20}H_{38}$, one of which is a liquid. The other *dimenthyl*, which dissolves readily in ether or benzene, and to a slight extent in alcohol, crystallises from hot alcohol in drusy masses, and from cold alcohol or benzene in well-developed, many-faced crystals which melt at 105·5—106°, and boil at 185—186° under 21 mm. pressure; it has the normal molecular weight in freezing benzene, and in a 19·4 per cent. benzene solution $[\alpha]_D$ $-51°18'$. The same products, namely, menthene, menthane, and liquid and crystalline dimenthyls, are obtained on boiling with sodium, ethereal solutions of the menthyl chloride and iodide, obtained by heating the corresponding haloid hydracids with menthol. It has been found by various investigators that when menthyl chloride is boiled with alcoholic potassium hydroxide, it is partly decomposed, the remainder differing from the original by possessing a considerable lævorotatory power. By pushing the action of the alcoholic potassium hydroxide until the menthyl chloride remaining is no longer decomposed, a lævo-modification having constant properties and quite free from menthene is obtained; the same menthyl chloride may also be prepared by boiling the ordinary chloride with aniline. It has $[\alpha]_D$ $-50°56'$ and a sp. gr. 0·9555 at 0°/0°, 0·9411 at 20°/0°, and 0·943 at 15°/15°; it boils at 109—110° at 30 mm. pressure. Slawinski (*loc. cit.*) gave for this compound $[\alpha]_D$ $-51°57'$, the sp. gr. 0·941 at 18°, and the boiling point 91—93° under a pressure of 13·5 mm. The homogeneity of this menthyl chloride is indicated by the fact that, when boiled in ethereal solution with sodium, it yields as sole product the crystalline dimenthyl described above. The optical activity of the menthyl chloride and of the dimenthyl derived from it shows that both these compounds must be of a secondary nature, and the formula of the latter must be represented by



$$CH_2<\begin{matrix}CHMe\cdot CH_2\\CH_2\cdot CHPr\end{matrix}>CH\cdot CH<\begin{matrix}CH_2\cdot CHMe\\CHPr\cdot CH_2\end{matrix}>CH_2.$$

Kondakoff and Lutschinin (Abstr., 1900, i, 104) supposed that the action of hydriodic acid on menthol yields tertiary menthyl iodide, but the formation of some crystalline dimenthyl when it is boiled in ethereal solution with sodium shows that some secondary compound is present. For preparing the tertiary halogen compound, the author uses von Baeyer's method of acting on an acetic acid solution of menthene with the halogen hydracid. The menthyl bromide thus obtained boils at 98—100° under 11—12 mm. pressure, and has the sp. gr. 1·167 at 15°/15° and 1·1663 at 20°/0°, Kondakoff (Abstr., 1895, i, 549) giving the boiling point 100—103° under 13 mm. pressure, and the density as 1·179 at 0° and 1·161 at 23°; it has a slight dextrorotation, due, possibly, to admixture with a small quantity of menthene. This tertiary menthyl bromide, as also the tertiary chloride obtained in a similar way, when boiled in ethereal solution with sodium, yields a practically inactive dimenthyl.

The author considers that the liquid dimenthyl just mentioned is probably a stereoisomeride of the crystalline compound.

Ethylmenthane,  $CH_2<\begin{matrix}CHMe\cdot CH_2\\CH_2\cdot CHPr\end{matrix}>CHEt$, prepared by the action of zinc ethyl on *l*-menthyl chloride, boils at 209—210° under 730 mm. pressure, has the sp. gr. 0·8275 at 0°/0°, 0·8146 at 20°/0°, and 0·8159 at 20°/20°, $[\alpha]_D$ − 12°15′, and is the first optically active naphthene obtained. T. H. P.

Action of Nitric Anhydride on Camphene. By Nicolaus I. Demjanoff (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 283—289).—The action of nitric anhydride on a chloroform solution of camphene yields an *acid*, $C_{10}H_{15}O_5N$, which separates from aqueous alcohol in long prisms, often grouped together in spherical aggregates, or in short, stout prisms melting at 140—141°, and swelling up, turning brown, and evolving gas at 165—170°; it decomposes potassium carbonate, giving a soluble potassium salt, and has the normal molecular weight in freezing acetic acid. The sparingly soluble *silver* salt was analysed. When reduced by means of tin and hydrochloric acid, or when heated with a concentrated aqueous solution of potassium hydroxide, the acid is converted into dehydrocamphenylic acid.

The first action of nitric anhydride on camphene is probably the formation of the nitric ester of camphene glycol, $C_{10}H_{16}O_6N_2$, which is afterwards transformed into the acid, $C_8H_{14}\colon C(O\cdot NO_2)\cdot CO_2H$, melting at 140—141°, just described. These results, together with those of the action of nitric acid and of nitrous anhydride on camphene, lend support to Wagner's formula, $C_8H_{14}\colon C\colon CH_2$, for camphene. T. H. P.

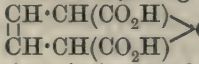
The Sugar obtained from Cerebrin. By Friedrich N. Schulz and Fritz Ditthorn (*Zeit. physiol. Chem.*, 1901, **32**, 425—427. Compare Abstr., 1890, 121).—It has been proved beyond doubt that the sugar obtained by the hydrolysis of cerebrin with sulphuric acid is galactose and not a galactosamine. J. J. S.

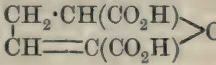
Chlorophyll. Degradation of Phyllocyanin to Hæmopyrrole. By Marcellus Nencki and Leo Marchlewski (*Ber.*, 1901, **34**, 1687—1690).—When phyllocyanin, in the form of its copper acetate salt, is reduced with hydriodic acid and phosphonium iodide, it yields hæmopyrrole (this vol., i, 434), which was isolated in the form of its mercurichloride. This fact confirms the close relationship of hæmatoporphyrin and phylloporphyrin. W. A. D.

Oxidation of Melaninic Acid. By Walter Jones and John Auer (*Amer. J. Physiol.*, 1901, **5**, 321—332).—Melaninic acid, obtained from the black pigment of horse-hair, was oxidised by means of potassium permanganate. Oxalic acid was found to be one of the principal end-products. No aromatic substance was found. The pigment is probably related to the proteids, but the predominant grouping in it is that which in the proteids gives rise to aliphatic amino-acids.

W. D. H.

Dehydromucic Acid. By HENRY B. HILL (*Amer. Chem. J.*, 1901, **25**, 440—445).—This paper is an introduction to the two following.

On reducing dehydromucic acid with sodium amalgam, Seelig (Abstr., 1879, 783) obtained two isomeric acids, $C_6H_6O_5$; although, as has been stated by Schrötter (Abstr., 1888, 1060), the acid of lower melting point or *a*-acid is the only direct product of reduction, it has not been found possible to avoid its partial conversion into that of higher melting point, the *β*-isomeride. The *a*-acid, being the first product of reduction, must have the structure  $\left.\begin{array}{l}CH\cdot CH(CO_2H)\\ \|\\ CH\cdot CH(CO_2H)\end{array}\right>O$, and the *β*-acid has probably the same constitution, since it is unstable in alkaline solution; the author considers that the former acid is the *cis*-form, whilst the latter is the inactive combination of the two active *cis-trans*-modifications. Both acids are optically inactive; the *β*-acid has been resolved into two optically active constituents by means of their cinchonine salts.

The *γ*-acid, which is the final product of the action of alkalis on the *a*- or *β*-acid, has the configuration  $\left.\begin{array}{l}CH_2\cdot CH(CO_2H)\\ |\\ CH{=\!=}C(CO_2H)\end{array}\right>O$, and can be separated into two optically active components. E. G.

Dehydromucic Acid and certain of its Derivatives. By ISAAC K. PHELPS and WILLIAM J. HALE (*Amer. Chem. J.*, 1901, **25**, 445—463).—Dehydromucic acid is obtained in a yield of 34·6 per cent., by heating potassium hydrogen saccharate with hydrobromic acid of sp. gr. 1·56 for 16 hours, whilst by the action of hydrobromic acid of sp. gr. 1·49 on mucic acid, a yield of 20·2 per cent. is produced. The statement of Schmidt and Cobenzl (Abstr., 1884, 1125), that the acid could be obtained by the action of heat on potassium mucate, could not be confirmed. Dehydromucic acid is soluble in water at 18° to the extent of 0·1 per cent., the barium salt 0·91 per cent., and the calcium salt 3·94 per cent.; the *potassium* salt crystallises with $1H_2O$. The *methyl* ester crystallises from water in lustrous leaflets and melts at 201—202° (corr.); the *ethyl* ester forms groups of needles and melts at 148—149° (corr.). The *amide* crystallises from hot water in long, slender needles and melts at 280—281° (corr.). The *dianilide* forms long, radiating needles and melts at 227—228° (corr.). *Dehydromucic diacetic anhydride*, $C_{10}H_8O_7$, obtained by the action of acetic anhydride on the acid, crystallises in colourless leaflets; it decomposes at about 150° with liberation of acetic anhydride and formation of *dehydromucic anhydride* as a crystalline sublimate; this substance is probably formed from 2 mols. of the acid, and is therefore represented by the formula $C_{12}H_4O_8$. When the acid chloride is heated with bromine, substitution does not take place. By the action of bromine on potassium dehydromucate, dibromofurfuran tetrabromide is obtained, and by the action of iodine, *diiodofurfuran* is formed, which crystallises in colourless plates and melts at 47°. If bromine is added to an alkaline solution of ethyl dehydromucate, δ-bromopyromucic acid is produced; the corresponding iodopyromucic acid could not be obtained in this manner.

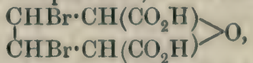
2 : 5-*Dibenzoylfurfuran*, obtained by heating a solution of dehydromucyl chloride in benzene with aluminium chloride, crystallises from

alcohol or light petroleum in lustrous needles, melts at 107° (corr.), sublimes at a higher temperature, and is readily soluble in benzene, chloroform, or glacial acetic acid; when it is heated with bromine water at 140° in a sealed tube, dibromomaleic and *o*-, *m*-, and *p*-bromobenzoic acids are produced. When 2 : 5-dibenzoylfurfuran is boiled with nitric acid of sp. gr. 1·4, a *substance*, $C_{18}H_{11}O_5N$, melting at 130—131° is produced, together with *o*-, *m*-, and *p*-nitrobenzoic acids, and a small quantity of a crystalline substance which melts at 194—195°. 2 : 5-Dibenzoylfurfuran *diphenylhydrazone* crystallises in needles and melts at 155—156° (corr.). The *dioxime* is obtained in two modifications, both of which are readily soluble in acetone or ethyl acetate; the α-dioxime crystallises in long, slender needles, and when heated melts at 213—214° and is partially converted into the β-form; the β-modification forms groups of minute, irregular plates and melts at 243—245°.

E. G.

Reduction of Dehydromucic Acid. By Henry B. Hill and Alvin S. Wheeler (*Amer. Chem. J.*, 1901, 25, 463—485. Compare preceding abstracts).—The two isomeric acids obtained by Seelig by the reduction of dehydromucic acid with sodium amalgam, were separated by him by means of their barium salts. After the removal of these salts, the authors have obtained the salt of a third or γ-acid from the mother liquor; they have also found that these acids may be more readily separated by means of their lead salts.

α-Dihydrofurfuran-2 : 5-dicarboxylic acid is almost exclusively obtained if the reduction is carried on at 0° and a rapid stream of carbon dioxide is passed into the solution; it is readily soluble in water, alcohol, or ether, crystallises in plates or needles, and melts at 149—150° (corr.). The solubility of the barium salt in water at 18° is 0·2 per cent.; the calcium salt crystallises with $1\frac{1}{2}H_2O$; the *lead* salt, with $1H_2O$, is soluble in water to the extent of 0·046 at 20°, and 1·03 per cent. at 99·5°. When the acid is heated at 190° in a current of hydrogen, carbon monoxide is evolved, and a sublimate is obtained consisting of the original acid together with a small quantity of slender needles melting at 130°, which are probably pyromucic acid. On oxidation with nitric acid or alkaline potassium permanganate, the acid is converted into dehydromucic and oxalic acids. If the acid is heated with bromine in a sealed tube at 140°, hydrogen bromide and dehydromucic acid are produced, whilst by the action of bromine on an aqueous solution at the ordinary temperature, a *dibromide*,

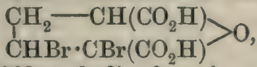


$$\left.\begin{array}{l}CHBr\cdot CH(CO_2H)\\ CHBr\cdot CH(CO_2H)\end{array}\right>O,$$

is obtained which crystallises in prisms containing $1H_2O$, melts at 112—113°, and is readily soluble in alcohol or ether; when left over sulphuric acid, it becomes anhydrous and melts at 147—148° (corr.). By the action of sodium amalgam or zinc dust on the dibromide, the α-acid is regenerated; when its aqueous solution is treated with barium hydroxide and left for 24 hours, barium pyromucate, bromide, and carbonate are produced. If an aqueous solution of the α-acid is saturated with chlorine, *α-chlorohydroxytetrahydrofurfuran-2 : 5-dicarboxylic acid*, $C_6H_7O_6Cl$, is formed, which crystallises in prisms, decomposes at

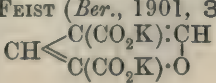
209—210° (corr.), dissolves readily in water, alcohol, or acetone, and when treated with acetic anhydride yields a well crystallised product.

β-Dihydrofurfuran-2 : 5-dicarboxylic acid, which may be obtained by boiling a solution of the α-acid with sodium hydroxide, or directly from dehydromucic acid by modifying slightly the method of reduction, crystallises in needles, melts at 178—179° (corr.), and is readily soluble in alcohol. The solubility of the barium salt in water is 1·40 per cent. at 20°; the calcium salt crystallises with $2\frac{1}{2}H_2O$; the *lead* salt with $1H_2O$, is soluble in water to the extent of 0·0013 per cent. at 20°, and 0·022—0·032 per cent. at 99·5°. When the β-acid is oxidised with nitric acid, dehydromucic and oxalic acids are formed, whilst by the action of alkaline potassium permanganate, oxalic acid only is produced. The *dibromide* dissolves readily in alcohol or ether, decomposes at 213—214° (corr.), and is readily reduced to the β-acid by means of sodium amalgam; when an aqueous solution of this compound is treated with barium hydroxide, barium pyromucate, bromide, and carbonate are produced. By the action of chlorine on the β-acid, the *compound* $C_6H_7O_6Cl,1\frac{1}{2}H_2O$ is obtained, which crystallises in truncated prisms, melts at 95°, and reacts with acetic anhydride to form a crystalline product.

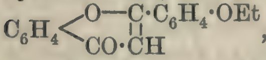
*γ-Dihydrofurfuran-*2 : 5-*dicarboxylic acid*, obtained by boiling the β-acid for a long time with sodium hydroxide solution, crystallises in stellate groups of plates, decomposes at 190—200° according to the rate of heating, and dissolves readily in alcohol or hot glacial acetic acid. Whilst the α- and β-acids are not affected by sodium amalgam, the γ-acid is converted into the two isomeric tetrahydrofurfuran-2 : 5-carboxylic acids recently described by Lean (Trans., 1900, 77, 103). The γ-acid is readily oxidised by nitric acid or alkaline potassium permanganate with formation of dehydromucic and oxalic acids. The *dibromide*,  $\left.\begin{array}{l}CH_2\text{——}CH(CO_2H)\\ |\\ CHBr\cdot CBr(CO_2H)\end{array}\right>O$, crystallises in prisms, decomposes at about 200°, and dissolves in water or alcohol to form unstable solutions; by the action of barium hydroxide on this compound, pyromucic acid is not produced.
E. G.

Insoluble Coumarone- and Indene-Resins. By GUSTAV KRAEMER and ADOLF SPILKER (*Ber.*, 1901, 34, 1887—1889. Compare Störmer, Abstr., 1900, i, 650).—The analyses previously given (Abstr., 1900, i, 656) were obtained from a soluble resin, and fresh analyses of insoluble coumarone-resins prove that combined sulphur is always present (8·5—9·94 per cent.). When subjected to destructive distillation, it yields sulphur, sulphur dioxide, hydrogen sulphide, and practically the same products as were obtained from the soluble resin. The resin obtained from indene (*loc. cit.*) was in reality derived from coumarone and methylcoumarone contained in the indene.

J. J. S.

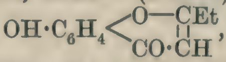
Conversion of Coumalic Acid into an Isomeride of Dehydromucic Acid. By FRANZ FEIST (*Ber.*, 1901, 34, 1992—1996).—*Furfuran-*2 : 4-*dicarboxylic acid*,  $CH\!<\!\begin{array}{l}C(CO_2K){:}CH\\ \qquad\qquad\;\; |\\ C(CO_2K)\cdot O\end{array}$ $+ H_2O$, prepared by the action of aqueous potassium hydroxide on methylbromocoumalate, crystallises from water in glistening flakes, melts at 266°, and sublimes slowly below the melting point. The *calcium*, *barium*, and *silver* salts are described. The acid decolorises permanganate and bromine water, but does not reduce ammoniacal silver solutions, and does not lose carbon dioxide when heated alone at 270°, or with acetic acid at 170°. The *methyl* ester crystallises from methyl alcohol in glistening prisms and melts at 109—110°. T. M. L.

3′-Hydroxyflavone. By STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Ber.*, 1901, **34**, 1690—1693).—m-*Ethoxyacetophenone*, prepared by ethylating the corresponding phenol, is a colourless oil which boils at 255°, and readily condenses with ethyl *o*-methoxybenzoate in presence of sodium to form ω-o-*methoxybenzoyl*-3-*ethoxyacetophenone*. $OMe\cdot C_6H_4\cdot CO\cdot CH_2\cdot CO\cdot C_6H_4\cdot OEt$, which crystallises from dilute alcohol in white needles and melts at 63°; when the latter is added to warm hydriodic acid, it loses alcohol (1 mol.), and yields 3′-*ethoxyflavone*,



$C_6H_4{<}\begin{matrix}O—C\cdot C_6H_4\cdot OEt\\ \quad\;\, \| \\ CO\cdot CH\end{matrix}$, which forms white needles, melts at 118°, and, when boiled for several hours with the concentrated acid, loses its ethoxyl group, giving 3′-*hydroxyflavone*. This crystallises from dilute alcohol in broad, white prisms, melts at 208°, and yields a sparingly soluble, crystalline *sodium* salt; the *acetyl* derivative forms white needles or prisms and melts at 97°. W. A. D.

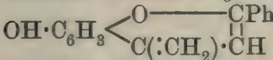
Syntheses in the Chromone Group. By STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Ber.*, 1901, **34**, 1693—1698. Compare Bloch and von Kostanecki, Abstr., 1900, i, 308, 502, and Crivelli and von Kostanecki, *ibid.*, i, 668).—[With W. ORTH.]—ω-*Propionyl*-2 : 5-*diethoxyacetophenone*, $C_6H_3(OEt)_2\cdot CO\cdot CH_2\cdot COEt$, obtained by the sodium ethoxide condensation of quinacetophenone diethyl ether with ethyl propionate, crystallises from dilute alcohol in colourless leaflets and melts at 49°; when heated for 2 hours with hydriodic acid of sp. gr. 1·96, alcohol (1 mol.) is eliminated, and 6-*hydroxy*-2-*ethylchromone*,

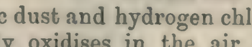


$OH\cdot C_6H_4{<}\begin{matrix}O—CEt\\ \quad\;\, \| \\ CO\cdot CH\end{matrix}$, formed. It separates from alcohol in long, spear-shaped crystals, melts at 165°, and gives a solution in concentrated sulphuric acid which shows a greenish-blue fluorescence. The *acetyl* derivative forms white leaflets and melts at 92—93°; the *methyl* ether crystallises from alcohol in rhombic plates melting at 87—88°, and the *ethyl* ether from light petroleum in prisms melting at 65—66°. Both of the ethers show a greenish-blue fluorescence in concentrated sulphuric acid solution. When the ethyl ether is heated with alcoholic sodium ethoxide for several hours at 100°, it is resolved into quinacetophenone monoethyl ether and propionic acid.

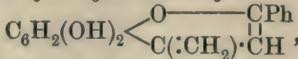
[With L. PAUL.]—ω-*Propionyl*-2 : 4-*diethoxyacetophenone*, obtained by condensing ethyl propionate and resacetophenone diethyl ether, crystallises from dilute alcohol in prisms, melts at 74—75°, and with hydriodic acid yields initially 7-*ethoxy*-2-*ethylchromone*, and finally 7-*hydroxy*-2-*ethylchromone*; the former crystallises from dilute alcohol in sheaves of needles (+ $1H_2O$) melting at 83—84°, the latter in short prisms melting at 186°. 7-*Acetoxy-2-ethylchromone* forms white prisms and melts at 67—68°. All these compounds show a violet-blue fluorescence when dissolved in concentrated sulphuric acid.

[With W. WINTER.]—ω-*Butyryl*-2 : 4-*diethoxyacetophenone*, from ethyl butyrate and resacetophenone diethyl ether, forms thick, white needles and melts at 60—61°. 7-*Hydroxy-2-propylchromone* crystallises from alcohol in thick, colourless needles and melts at 148°; the *acetyl* derivative forms white leaflets and melts at 64—65°. W. A. D.

Derivatives of 1 : 4-Benzopyranol, the Parent Substance of a new class of Colouring Matters. II. By CARL BÜLOW and HERMANN WAGNER (*Ber.*, 1901, **34**, 1782—1804. Compare this vol., i, 400).—Resorcinol condenses with benzoylacetone in presence of hydrogen chloride to form 7-*hydroxy-2-phenylanhydro-4-methyl*-1 : 4-*benzopyranol*,  $OH\cdot C_6H_3<\begin{matrix}O\text{——}CPh\\ C(:CH_2)\cdot CH\end{matrix}$; the *hydrochloride*, $C_{16}H_{12}O_2,HCl,H_2O$, crystallises from dilute alcohol containing a little free hydrogen chloride in yellow needles or in brownish-yellow tablets, which are less readily soluble than the needle-shaped modification; it becomes red at about 140°, and blackens at 280°. The *anhydro-base*, $C_{16}H_{12}O_2$, is a dark-red, amorphous powder, and chars, without melting, when heated. The substance is hydrolysed by a 10 per cent. solution of potassium hydroxide to acetophenone and resacetophenone. The *picrate* of the anhydro-base separates in yellow prisms when picric acid is added to a solution of the hydrochloride in a mixture of alcohol and acetic acid. The *acetyl* derivative, $C_{18}H_{14}O_3$, exists in two modifications; when prepared in the cold by the action of acetic anhydride on an alkaline solution of the base, it is obtained as a white, amorphous powder, which sinters at 155—160° but has no definite melting point, dissolves readily in most organic solvents, and is converted by heating with acetic anhydride and sodium acetate into the coloured modification; this is best prepared by heating the base with acetic anhydride and sodium acetate, sinters above 300°, is insoluble in most organic solvents, but dissolves in hot aniline, pyridine, or nitrobenzene, and crystallises from the latter in brown flakes with a dark green, metallic lustre. The *methyl* ether, $C_{17}H_{14}O_2$, also exists in two modifications; the amorphous form, prepared by the action of methyl sulphate on an alkaline solution of the base, is obtained as a white, flocculent precipitate, is readily soluble in most solvents, and sinters at 120—125°; the crystalline modification, prepared by the action of methyl iodide and sodium methoxide, sinters at 261—263°, is only slightly soluble in most solvents, but dissolves in aniline, nitrobenzene, and pyridine, and crystallises from a mixture of pyridine and methyl alcohol in brownish-red needles with a dark green, metallic lustre.

7-*Hydroxy-2-phenyl-4-methylbenzopyran*,  $OH\cdot C_6H_3<\begin{matrix}O\text{——}CPh\\ CHMe\cdot CH\end{matrix}$, prepared by reducing the colour base with zinc dust and hydrogen chloride, is a yellowish-white powder which readily oxidises in the air when moist, dissolves easily in organic solvents, and sinters at 155—160°; the *acetyl* derivative, $C_{18}H_{16}O_3$, is a white, amorphous powder, dissolves in most solvents, does not oxidise in the air, and sinters at 115—120°.

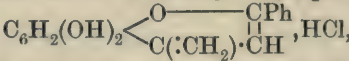
5 : 7-*Dihydroxy-2-phenylanhydro-4-methyl*-1 : 4-*benzopyranol*,



$$C_6H_2(OH)_2<\begin{array}{l}O\text{———}CPh\\ C(:CH_2)\cdot CH\end{array},$$

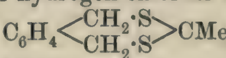
is prepared by condensing phloroglucinol with benzoylacetone; the *hydrochloride*, $C_{16}H_{12}O_3,HCl,H_2O$, crystallises in stout, orange-red needles, is insoluble in most organic solvents, and blackens between 200° and 250°; the *anhydro-base*, $C_{16}H_{12}O_3$, is a reddish-brown, amorphous powder, readily soluble in most solvents, and blackens when heated above 100°; when hydrolysed with aqueous potassium hydroxide, it gives acetophenone and phloroacetophenone. The *picrate* crystallises from dilute alcohol in glistening, orange-red needles. The *acetyl* derivative was obtained as a brownish-white, amorphous powder.

The *hydrochloride* of 7 : 8-*dihydroxy-2-phenylanhydro-4-methyl*-1 : 4-*benzopyranol*,



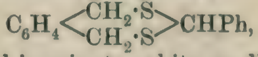
$C_6H_2(OH)_2<\begin{array}{l}O\text{———}CPh\\ C(:CH_2)\cdot CH\end{array},HCl$, prepared by condensing pyrogallol with benzoylacetone, crystallises in minute, reddish-brown, rhombic tablets, and chars when heated above 200°; the *base*, $C_{16}H_{12}O_3$, is a black, crystalline powder, which dissolves to a violet solution in most organic solvents; boiling with aqueous potassium hydroxide hydrolyses it to acetophenone and gallacetophenone. The *picrate*, $C_{22}H_{15}O_{10}N_3$, forms dark violet, hexagonal tablets. The *diacetyl* derivative, $C_{20}H_{16}O_5$, prepared by the action of sodium acetate and acetic anhydride on the base, resembles the crystalline monoacetoxy-compound; it is insoluble in most solvents, but crystallises from nitrobenzene in reddish-brown, transparent flakes with a dark green, metallic lustre. T. M. L.

Ring Compounds containing Sulphur. By WILHELM AUTENRIETH and R. HENNINGS (*Ber.*, 1901, 34, 1772—1778).—*o*-Xylylene mercaptan, $C_6H_4(CH_2\cdot SH)_2$, condenses with acetone in presence of hydrogen chloride to cyclo-*o*-*xylylene*-1 : 3-*dithio*-2-*dimethylmethylene*,



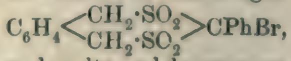
$C_6H_4<\begin{array}{l}CH_2\cdot S\\ CH_2\cdot S\end{array}>CMe_2$, which crystallises from alcohol in glistening flakes, and is not reduced to the mercaptan by zinc and dilute hydrogen chloride. The *disulphone*, $C_{11}H_{14}S_2O_4$, is a white, crystalline powder which melts above 300°, and is insoluble in water and most organic solvents, but soluble in nitric and sulphuric acids.

cyclo-*o*-*Xylylene*-1 : 3-*dithio*-2-*phenylmethylene*,



$$C_6H_4<\begin{array}{l}CH_2\cdot S\\ CH_2\cdot S\end{array}>CHPh,$$

crystallises from alcohol in minute, white needles, melts at 170°, and is not reduced to the mercaptan by zinc and dilute hydrogen chloride. The *disulphone*, $C_{15}H_{14}O_4S_2$, melts above 300°, is insoluble in most solvents, but crystallises from a mixture of acetone and water in glistening, white prisms and minute needles, and dissolves unchanged in sulphuric acid. The *bromo*-derivative,



$C_6H_4<\begin{array}{l}CH_2\cdot SO_2\\ CH_2\cdot SO_2\end{array}>CPhBr$, crystallises from acetone in glistening flakes and melts and decomposes at 268°. T. M. L.

Conversion of Dextrorotatory Arginine into its Optically Inactive Isomeride. By FR. KUTSCHER (*Zeit. physiol. Chem.*, 1901, **32**, 476—478).—*i*-Arginine is readily produced by the tryptic fermentation of fibrin. *r*-Arginine may be obtained by heating *d*-arginine with concentrated sulphuric acid to incipient boiling, or by dehydrating *d*-arginine nitrate at 80°, and then heating at 210—220° for 15—20 mins. J. J. S.

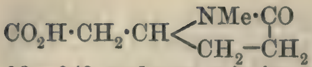
Oxidation Products of Arginine. II. By FR. KUTSCHER (*Zeit. physiol. Chem.*, 1901, **32**, 413—418. Compare this vol., i, 403).—The products obtained by the oxidation of arginine are *γ-guanidinebutyric acid*, $NH_2\cdot C(NH)\cdot NH\cdot[CH_2]_3\cdot CO_2H$, and the oxidation products of this, namely, guanidine and succinic acid. γ-Guanidinebutyric acid forms a *hydrochloride*, $C_5H_{11}O_2N_3,HCl$, melting at 184° (uncorr.), and readily soluble in water. These results confirm Schulze and Winterstein's (Abstr., 1898, i, 281; 1899, i, 107; 1900, i, 110) and Ellinger's (*ibid.*, 1900, i, 143) conclusions regarding the constitution of arginine. J. J. S.

1-Methyl-2-vinylpiperidine. By MARTIN HEIDRICH (*Ber.*, 1901, **34**, 1889—1893).—1-Methyl-2-vinylpiperidine, which was prepared in small quantity by Ladenburg (Abstr., 1893, i, 426), has been obtained on a larger scale by heating 1-methylpipecolylalkine (1-methyl-2-hydroxyethylpiperidine) with concentrated hydrochloric acid in sealed tubes at 165—175°. It is a colourless oil with a strong odour resembling that of coniine, boils at 60° under 12 mm. pressure, and is readily volatile in a current of steam; it dissolves slightly in water, more readily in alcohol or ether, and when kept for some time, or when distilled at the ordinary pressure, it polymerises. Its *platinichloride*, $(C_8H_{15}N)_2,H_2PtCl_6$, forms bushy masses of small, shining, reddish needles or pyramidal crystals which dissolve readily in hot water and melt at 188°. The *aurichloride* separates from water in small, deformed crystals melting at 115—120°.

Reduction of 1-methyl-2-vinylpiperidine with tin and hydrochloric acid yields 1-methyl-2-ethylpiperidine (see Ladenburg, Abstr., 1898, i, 339), which gives a *mercurichloride*, $C_8H_{17}N,HCl,6HgCl_2$, melting at 201—206°, and a *picrate* melting at 175—176°.

1-*Methyl-2-pipecolylalkine iodide hydriodide* [1-*methyl-2-iodoethylpiperidine hydriodide*], $C_5NH_9Me\cdot CH_2\cdot CH_2I,HI$, prepared by the action of phosphorus and hydriodic acid, melts at 163° when deposited from benzene, and at 155—158° when obtained from alcohol by the addition of ether; it forms pale yellow needles readily soluble in water, alcohol, chloroform, or benzene. When repeatedly shaken with freshly precipitated silver hydroxide (2 mols.), the hydriodide (1 mol.) yields mainly 1-methyl-2-hydroxyethylpiperidine with a small quantity of 1-methyl-2-vinylpiperidine. T. H. P.

Synthesis of Ecgonic Acid. By RICHARD WILLSTÄTTER and CHARLES HOLLANDER (*Ber.*, 1901, **34**, 1818—1819).—Δ^{β}-Hydromuconic acid combines with hydrogen bromide to form *β-bromoadipic acid*, $CO_2H\cdot CH_2\cdot CHBr\cdot CH_2\cdot CH_2\cdot CO_2H$, which crystallises in prisms melting at 147°. When heated with a solution of methylamine in benzene, this acid gives an almost quantitative yield of ecgonic acid,



$CO_2H\cdot CH_2\cdot CH\!<\!\begin{array}{l}NMe\cdot CO\\ CH_2-CH_2\end{array}$; the synthetic (racemic) acid melts at 93—94°, and agrees in its properties and salts with the acid obtained from tropine. The *copper* salt is very soluble in water and is precipitated by acetone in emerald-green prisms.

This synthesis affords the first direct proof of the presence of the pyrrolidine ring in tropine and ecgonine. A. H.

Action of Cuminaldehyde on α-Picoline (2-Methylpyridine). By P. Backe (*Ber.*, 1901, **34**, 1893—1896).—When cuminaldehyde and α-picoline are heated together in a sealed tube, the following two products are obtained.

(1.) 2-*Hydroxy-β*-p-iso*propylphenylethylpyridine*,

$C_5NH_4\cdot CH_2\cdot CH(OH)\cdot C_6H_4Pr^\beta$,

which is formed when the two compounds are heated at 140° in presence of water, crystallises from alcohol in white needles having a satiny lustre and melting at 80°; it is readily soluble in alcohol, ether, acetone, or benzene. The *platinichloride*, melting at 201°, the *aurichloride* (with $1H_2O$), melting at 107—108°, the *picrate*, melting at 135°, and the *ferrocyanide* were analysed.

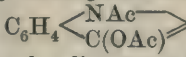
(2.) iso*Propyl-α-stilbazole*, $C_5NH_4\cdot CH{:}CH\cdot C_6H_4Pr^\beta$, is obtained when cuminaldehyde and picoline are heated at 240—250° in a sealed tube; it separates from ether as a white, crystalline mass melting at 47°, and dissolves readily in ether or alcohol but only slightly in acids. Its *mercurichloride*, melting at 143°, *platinichloride* (with $2H_2O$), melting at 170°, and its *picrate*, melting at 189—190°, were prepared. It gives a *dibromide*, $C_{16}H_{17}NBr_2$, separating from alcohol in snow-white, sparkling leaflets melting at 159—160°. On reduction with sodium and alcohol, the base yields iso*propyl-α-stilbazoline*, $C_5NH_{10}\cdot CH_2\cdot CH_2\cdot C_6H_4Pr^\beta$, which is a colourless oil boiling at 300—305° under the ordinary pressure, at 176° under 16 mm., and at 110° under 10 mm. pressure; on exposure to air, it turns yellowish, and when kept cold it slowly deposits very deliquescent, white needles; in presence of water, the base has a strongly alkaline reaction towards litmus paper. Its *hydrochloride*, melting at 150°, *hydrobromide*, melting at 148°, and *platinichloride* (with $4H_2O$), melting at 85°, were analysed. T. H. P.

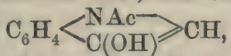
o-Nitrophenyl-5-ethyl-2-picolylalkine [5-β-Hydroxy-β-o-nitrophenylethyl-1-ethylpyridine] and its Derivatives. By W. Castner (*Ber.*, 1901, **34**, 1897—1901).—5-*β-Hydroxy-β*-o-*nitrophenylethyl-2-ethylpyridine*, $NO_2\cdot C_6H_4\cdot CH(OH)\cdot CH_2\cdot C_5NH_3Et$, prepared by heating molecular proportions of *o*-nitrobenzaldehyde and aldehyde-collidine with water in a sealed tube at 150°, separates from dilute alcohol in silky, white needles which melt at 110° and dissolve readily in alcohol or acetone and to a less extent in ether; its *aurichloride*, melting at 138°, *platinichloride*, melting at 161°, and *mercurichloride* were analysed. Reduction of the base with mild reducing agents gives a small yield of the corresponding *amino*-compound, $C_{15}H_{18}ON_2$, which crystallises from dilute alcohol in small, yellow needles melting at 76° and dissolving in alcohol, ether, or acetone; its *hydrochloride* melts at 85°, its *aurichloride* at 117°, and its *platinichloride* at 134°.

When the nitro-compound is reduced with sodium and alcohol, both the pyridine nucleus and the nitro-group undergo reduction, giving rise to a *base*, $NH_2 \cdot C_6H_4 \cdot CH(OH) \cdot CH_2 \cdot C_5NH_9Et$, which is obtained as a yellow oil; the *platinichloride* melting and decomposing at 126°, the *mercurichloride*, and the *aurichloride* were analysed.

5-*β-Hydroxy-β-phenylethyl-2-ethylpyridine*, $OH \cdot CHPh \cdot CH_2 \cdot C_5NH_3Et$, prepared by the interaction of benzaldehyde and aldehyde-collidine in presence of water in a sealed tube at 150°, separates from water in white, well-formed crystals melting at 88°, and is readily soluble in alcohol or acetone and to a less extent in ether; the *aurichloride*, melting at 111°, and *platinichloride* were analysed. T. H. P.

Constitution of the Bases formed by the Action of Alkyl Iodides on the Indoles. By Giuseppe Plancher (*Gazzetta*, 1901, **31**, i, 280—284).—A reply to Brunner's claim of priority in this matter (see this vol., i, 407). T. H. P.

Acyl Derivatives of Indoxyl and of Indoxylic Acid. By Daniel Vorländer and B. Drescher (*Ber.*, 1901, **34**, 1854—1860).—[With F. Teller.]—*Methyl acetylindoxylate* melts at 143—144°, the corresponding *ethyl* ester at 136°. *Methyl benzoylindoxylate* crystallises in flat needles melting at 160° and the *ethyl* ester at 163°. The *phenyl cyanate* derivative of ethyl indoxylate melts at 187—189°, and is gradually decomposed when boiled with alcohol. *Methyl diacetylindoxylate*,  $C_6H_4<\begin{matrix}NAc\\C(OAc)\end{matrix}>C \cdot CO_2Me$, obtained by the action of acetic anhydride and sodium acetate, crystallises in plates melting at 83—84°, and the *ethyl* ester in needles melting at 82°. Acyl derivatives of indoxylic acid may readily be obtained by shaking alkaline solutions of the acid with acid anhydrides or chlorides; the acyl compounds thus obtained are identical with those formed by acylating the dry acid in the absence of alkali. *Acetylindoxylic acid* melts and decomposes at 175°, and gives a dark colour with ferric chloride. *Propionylindoxylic acid*, $C_{12}H_{11}O_4N$, melts at 163°, and *benzoylindoxylic acid* at 196°.

1-*Acetylindoxyl*,  $C_6H_4<\begin{matrix}NAc\\C(OH)\end{matrix}>CH$, obtained when indoxyl is left in contact with acetic anhydride for half an hour, crystallises from hot water in flat needles, melts at 136°, gives no colour with ferric chloride, and is soluble in alkalis. When its dilute potassium hydroxide solution is shaken with acetic anhydride, diacetylindoxyl melting at 82° is formed. 3-*Acetylindoxyl*, obtained by the action of acetic anhydride on alkaline solutions of indoxyl, crystallises in plates, melts at 126°, and its alcoholic solution gives no coloration with ferric chloride, but an acetic acid solution develops a dark violet-red colour with a little concentrated nitric acid or bromine water; it is not so readily further acetylated as the 1-compound. 1-*Nitroso-3-acetylindoxyl* crystallises in pale yellow needles, melts at 83°, and is insoluble in cold alkalis.

3 : 3′-*Dipropionyl-indigo-white*, $C_{22}H_{20}O_4N_2$, melts and partially decomposes at 218°; the *dibenzoyl* compound decomposes at about 240°, and on oxidation yields brownish-red crystals of dibenzoylindigo, which decompose above 200°. J. J. S.

Constitution of Indigo-carmine. By DANIEL VORLÄNDER and PHILIPP SCHUBART (*Ber.*, 1901, **34**, 1860—1863. Compare Schlieper, *Annalen*, 1861, **120**, 1).—Tolyl-*o*-glycine-*p*-sulphonic acid,

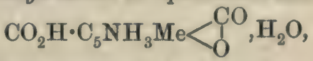
$$SO_3H\cdot C_6H_3Me\cdot NH\cdot CH_2\cdot CO_2H,$$

obtained by the oxidation of *o*-aminotoluene-*p*-sulphonic acid (*Annalen*, 1869, **155**, 8) with alkali chlorates, yields a *monosodium* salt, $C_9H_{10}O_5NSNa,5H_2O$, and a *potassium* salt, $C_9H_{10}O_5NSK,H_2O$. When oxidised in alkaline solution with permanganate, it yields 4-*sulphophenyl*-2-*glycine*-1-*carboxylic acid*, $SO_3H\cdot C_6H_3(CO_2H)\cdot NH\cdot CH_2\cdot CO_2H$, the *monopotassium* salt of which contains $2H_2O$. The dehydrated salt after condensation with acetic anhydride and sodium acetate, and treatment with dilute alkali, yields an isomeride of indigo-carmine.

Indigo-carmine itself may be obtained by similar methods from 6-aminotoluene-*m*-sulphonic acid (Neville and Winther, Trans., 1880, **37**, 625), and must therefore contain the sulphonic acid groups in ortho-positions to the carbonyl groups.

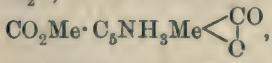
The *monosodium* salt of 5-*sulphophenylglycine*-1-*carboxylic acid* contains $4H_2O$, but the potassium salt is anhydrous. J. J. S.

Betaine of Quinolinic Acid. By ALFRED KIRPAL (*Monatsh.*, 1901, **22**, 361—374).—The methylbetaine of quinolinic acid is not obtained when the acid is heated with methyl alcohol and methyl iodide. Quinolinic anhydride and methyl iodide combine when heated at 100° to form an additive methiodide, $C_5NH_4MeI{<}\begin{matrix}CO\\CO\end{matrix}{>}O$; the latter, when dissolved in hot water and treated with silver oxide, becomes converted into the *methylbetaine* of quinolinic acid,



$$CO_2H\cdot C_5NH_3Me{<}\begin{matrix}CO\\|\\O\end{matrix},H_2O,$$

which crystallises in large, monoclinic plates [$a:b:c=0·556:1:2·019$, $\beta=105°·2'$] melting and decomposing at 151°. It is a strong monobasic acid which rapidly decomposes when suspended in boiling alcohol into carbon dioxide and trigonelline.

The *calcium* salt, $(C_8H_6O_4N)_2Ca,3H_2O$, and the *silver* salt, with H_2O, both form short prisms. The *methyl* ester of the betaine,  $CO_2Me\cdot C_5NH_3Me{<}\begin{matrix}CO\\|\\C\end{matrix}$, prepared from the methiodide of quinolinic anhydride and methyl alcohol, or from the α-methyl ester of quinolinic acid and methyl iodide, or by the action of methyl iodide on the silver salt of the betaine, crystallises in four- or six-sided plates melting and decomposing at 163°. The *ethyl* ester forms large, lustrous leaflets melting and decomposing at 160°. The *amide*, prepared by the action of ammonia on the methyl ester, crystallises in yellowish, quadratic plates or pyramids with H_2O, which becomes coloured at 200° and decomposes at 230°.

The author concludes that in the betaine, anhydride formation has taken place between the nitrogen and the 3-carboxyl group, as the methyl ester can be obtained from the α-methyl ester of quinolinic acid.

The *methochloride* of quinolinic acid, $C_5NH_3MeCl(CO_2H)_2$, prepared by the action of hot concentrated hydrochloric acid on the betaine, crystallises in prismatic needles decomposing at 220°, and is converted by heating with alcoholic hydrochloric acid into the methochloride of nicotinic acid.

With thionyl chloride, the betaine reacts vigorously, producing the methochloride of quinolinic anhydride. K. J. P. O.

Oxidation of Indigo-white with Oxygen. By WILHELM MANCHOT and JOHANNES HERZOG (*Annalen*, 1901, **316**, 318—330. Compare Abstr., 1900, i, 30, and this vol., ii, 93).—When an alkaline solution of indigo-white, obtained from pure synthetical indigo by reduction with zinc dust and sodium hydroxide, is shaken with air, the primary oxidation takes place in accordance with the equation $C_{16}H_{12}O_2N_2 + O_2 = C_{16}H_{10}O_2N_2 + H_2O_2$. The hydrogen peroxide combines with alkali present forming the corresponding peroxide, and if this happens to be soluble, the following secondary action occurs, $C_{16}H_{12}O_2N_2 + H_2O_2 = C_{16}H_{10}O_2N_2 + 2H_2O$. This loss of peroxide occurs in the presence of the alkali hydroxides, ammonia, and even borax; when barium hydroxide is employed, the secondary change is entirely prevented, and the process then affords a means of estimating the indigo-white in an indigo vat. The amount of peroxide produced is found by treating the mixture with lead peroxide and sulphuric acid, the volume of oxygen evolved being a measure of the indigo-white present. Lead peroxide is employed in preference to alkali permanganate and ferricyanide because these reagents oxidise the indigo, yielding gaseous products. The results obtained are tabulated, and the paper contains a sketch of an apparatus suitable for this estimation. G. T. M.

Isomeric Hydrazones. By EUGEN BAMBERGER and OTTO SCHMIDT (*Ber.*, 1901, **34**, 2001—2017).—α-Nitroformaldehydephenylhydrazone, $NO_2\cdot CH:N_2HPh$ (Abstr., 1900, i, 566), melts sharply at 74·5—75·5° when heated from 70°, but when heated from 20° undergoes partial isomeric change, and does not liquefy completely at 75°; when reheated after being fused and allowed to solidify, it melts sharply at 84·5—85·5°, and consists entirely of the β-phenylhydrazone. The α-isomeride is only partially altered by benzene, chloroform, light petroleum, or ether, but is completely changed into the β-isomeride by absolute or dilute alcohol; the β-isomeride, on the other hand, is unaltered by alcohol, but is converted partially by benzene, and completely by chloroform or light petroleum, into the α-isomeride. Neither isomeride has any marked conductivity.

Phenylnitroformaldehydephenylhydrazone, $NO_2\cdot CPh:N_2HPh$ (Hollemann, Abstr., 1895, i, 455), is only known in one form melting at 101·5—102·5°.

β-Benzoylformaldehydephenylhydrazone, $CHBz:N_2HPh$, prepared from diazobenzene and benzoylacetic acid (Abstr., 1886, 62), crystallises from alcohol in golden-yellow flakes with a bronze-like lustre, and melts, according to the rate of heating, between 136° and 140°; it has a normal molecular weight in boiling alcohol, and is converted into the α-isomeride, partially when boiled with benzene, and completely when boiled with light petroleum. α-Benzoylformaldehydephenylhydrazone crystallises in rosettes of orange-coloured prisms or in hemimorphic crystals with a violet lustre, melts between

114° and 117°, has a normal molecular weight in boiling benzene solution, and is converted into the β-isomeride to a slight extent when boiled with benzene, but completely when boiled with alcohol or acetone. The α-hydrazone dissolves more readily in benzene or light petroleum than the isomeride, but there is no marked difference in the solubility of the two forms in acetone or alcohol. When heated above the melting point, both isomerides are converted into a mixture melting between 126° and 128°. A specimen of the α-isomeride was found after five years to have passed completely at the ordinary temperature into the β-isomeride. Benzoylformaldehydephenylhydrazone is a feeble acid; the *sodium* salt forms small red needles, and is decomposed by atmospheric carbon dioxide and by water; acids usually convert it into a mixture of the α- and β-isomerides, but in one case the β-isomeride was alone produced.

*β-Benzoylformaldehyde-*o*-nitrophenylhydrazone*,

$$CHBz{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2,$$

prepared from *o*-nitrophenyldiazonium acetate and potassium benzoylacetate, crystallises from a mixture of alcohol and acetone in glistening, golden needles, melts at 145·5—146·5° when heated from 100°, but at 141·5—142·5° when heated from 20°, and has a normal molecular weight in freezing benzene. When a solution of the β-hydrazone in acetic acid, acetone, or benzene is allowed to evaporate, the residue consists partly of needles of the *α-hydrazone* melting between 113° and 117°, but on recrystallisation the β-hydrazone is reproduced. The α-hydrazone dissolves more readily than the β-hydrazone in acetone or benzene, or in warm alkaline hydroxides. When heated above the melting point, the α-hydrazone is converted very largely into the β-hydrazone, and remelts at 139—140°, and a specimen which had been kept at atmospheric temperature during 3½ years also melted at 137—138°, and only sintered very slightly at 114°. A mixture of isomerides was obtained by dissolving in alcoholic sodium ethoxide and pouring into ice-cold hydrochloric acid.

*Di-*m*-dinitroformazylphenylketone*,

$$NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}CBz{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2,$$

which is formed as a by-product in the action of *m*-nitrophenyldiazonium acetate on potassium benzoylacetate, separates from xylene in dark red crystals and melts and decomposes at 210°. *α-Benzoylformaldehyde-*m*-nitrophenylhydrazone* crystallises from light petroleum or benzene in orange-yellow, metallic needles with a violet lustre, and melts at 139—140°; prolonged boiling with alcohol converts it into the *β-modification*, which crystallises in orange-brown needles with a blue-violet lustre and melts between 149° and 152°, or into a γ-modification which separates in dull, whitish-yellow nodules; boiling with light petroleum and benzene converts the β- (or γ-) modification into the α-, and a similar change takes place when the substance is fused; the β-modification does not appear to be soluble in benzene except by conversion into the α-modification.

*Benzoylformaldehyde-*p*-nitrophenylhydrazone* crystallises from xylene in glistening, sulphur-yellow flakes with a violet lustre, melts at 199—200°, and is not known in more than one modification.

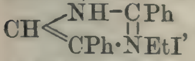
T. M. L.

Benzaldehydephenylhydrazone. By EUGEN BAMBERGER and JAC. GROB (*Ber.*, 1901, **34**, 2017—2023).—When benzaldehydephenylhydrazone suspended in glacial acetic acid is acted on at low temperatures by nitrous fumes, it is converted into phenylnitroformaldehydephenylhydrazone, $NO_2\cdot CPh\colon N\cdot NHPh$, identical with the substance obtained by V. Meyer from diazobenzene and phenylnitromethane (compare Abstr., 1899, i, 108, and von Pechmann, Abstr., 1893, i, 461). At the same time, nitration takes place in the benzene-ring, and a smaller amount of *phenylnitroformaldehyde*-p-*nitrophenylhydrazone*,

$$NO_2\cdot CPh\colon N\cdot NH\cdot C_6H_4\cdot NO_2,$$

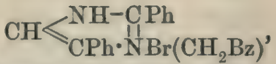
is produced; this was also prepared from sodium *iso*phenylnitromethane and *p*-nitrodiazobenzene nitrate; it crystallises from alcohol in minute, felted, silky, dark orange-red needles, and melts at 140·5° when heated from 135°. Phenyldiazonium and *p*-nitrophenyldiazonium nitrates are also found amongst the by-products of the action; they are probably produced by hydrolysis of the preceding compounds to benzaldehyde and the hydrazines, and the subsequent action of nitrous acid on the latter. T. M. L.

1 : 2 : 4-Substituted Iminazoles. By FRANZ KUNCKELL and P. DONATH (*Ber.*, 1901, **34**, 1829—1833. Compare Abstr., this vol., i, 293).—2 : 4-Diphenyliminazole readily forms an *ethiodide*,

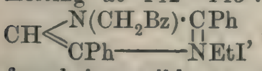


$CH\Big\langle\begin{matrix}NH-CPh\\ \Vert\\ CPh\cdot NEtI\end{matrix}$, which crystallises in small, white needles melting at 162°. Silver oxide converts this into 2 : 4-*diphenyl*-1-*ethyliminazole*, $C_{17}H_{16}N_2$, which is also formed by the action of ethyl iodide on silver diphenyliminazole, and crystallises in white needles melting at 194°. This compound again forms an *ethiodide*, $C_{19}H_{21}N_2I$, which melts at 154°. The corresponding *chloroacetic ester* derivative melts at 260°, and the *bromoacetic ester* compound at 236°.

2 : 4-*Diphenyliminazole phenacyl bromide*,



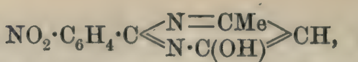
$CH\Big\langle\begin{matrix}NH-CPh\\ \Vert\\ CPh\cdot NBr(CH_2Bz)\end{matrix}$, readily formed from diphenyliminazole and phenacyl bromide, crystallises in white needles melting at 222°. On treatment with aqueous soda, hydrogen bromide is eliminated with the production of 2 : 4-*diphenyl*-1-*phenacyliminazole*, $C_{23}H_{18}ON_2$, which crystallises in plates melting at 142—143°. This substance readily forms an *ethiodide*,



$CH\Big\langle\begin{matrix}N(CH_2Bz)\cdot CPh\\ \Vert\\ CPh{-\!-\!-}NEtI\end{matrix}$, which melts at 202°. It has, however, been found impossible to obtain an additive compound with phenacyl bromide, diphenyliminazole phenacyl bromide being invariably produced.

Bromine converts diphenylphenacyliminazole into a *monobromo*-compound, which melts at 176°, and is not decomposed by dilute aqueous soda. It probably contains the bromine atom in the methylene group of the phenacyl residue, but this has not yet been definitely ascertained. A. H.

I. Pyrimidines and Cyanidines from Paranitrobenzamidine. II. Attempt to prepare *o*-Nitrobenzimino-ether. By THEODOR RAPPEPORT (*Ber.*, 1901, **34**, 1983—1992).—6-*Hydroxy*-2-p-*nitrophenyl*-

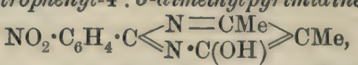
4-*methylpyrimidine*,  $\mathrm{NO_2\cdot C_6H_4\cdot C}\left<\begin{array}{l}\mathrm{N{=}CMe}\\ \mathrm{N\cdot C(OH)}\end{array}\right>\mathrm{CH}$, prepared by the action of sodium hydroxide on a mixture of ethyl acetoacetate and *p*-nitrobenzamidine hydrochloride, crystallises from acetic acid in minute needles, melts at 296°, is only sparingly soluble in most solvents, but dissolves readily in alkalis or acids, or in pyridine; the *silver* salt, $C_{11}H_8O_3N_3Ag$, forms a white precipitate.

6-*Hydroxy*-2-p-*aminophenyl*-4-*methylpyrimidine*, $C_{11}H_{11}ON_3$, prepared by reducing the nitro-compound with tin and hydrogen chloride, crystallises from dilute alcohol in microscopic, colourless prisms, melts at 233°, and dissolves in acids, alkalis, alcohol, or pyridine, but only sparingly in most other solvents; the *platinichloride*,

$$(C_{11}H_{11}ON_3)_2,H_2PtCl_6,$$

crystallises in yellow prisms and decomposes at 250°; the *silver* salt forms a white precipitate.

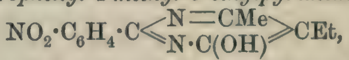
6-*Hydroxy*-2-p-*nitrophenyl*-4 : 5-*dimethylpyrimidine*,



$$\mathrm{NO_2\cdot C_6H_4\cdot C}\left<\begin{array}{l}\mathrm{N{=}CMe}\\ \mathrm{N\cdot C(OH)}\end{array}\right>\mathrm{CMe},$$

prepared from ethyl methylacetoacetate, crystallises from acetic acid in minute, colourless needles, does not melt at 305°, dissolves readily in acids or alkalis, but is only slightly soluble in most solvents. The *amino*-compound, $C_{12}H_{13}ON_3$, prepared by reducing the preceding compound, crystallises from dilute alcohol in yellowish, glistening flakes, melts and decomposes at 287°, and is readily soluble in alcohol; its *platinichloride*, $(C_{12}H_{13}ON_3)_2H_2PtCl_6$, forms glistening, yellow prisms.

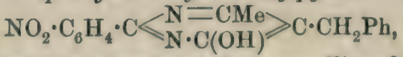
6-*Hydroxy*-2-p-*nitrophenyl*-4-*methyl*-5-*ethylpyrimidine*,



$$\mathrm{NO_2\cdot C_6H_4\cdot C}\left<\begin{array}{l}\mathrm{N{=}CMe}\\ \mathrm{N\cdot C(OH)}\end{array}\right>\mathrm{CEt},$$

prepared from ethyl ethylacetoacetate, crystallises from dilute acetic acid in long, yellowish, silky needles, dissolves readily in acids and alkalis, and melts and decomposes at 292°. The *amino*-compound, $C_{13}H_{15}ON_3$, prepared by reduction, crystallises from dilute alcohol in small, brownish prisms, is readily soluble in alcohol and in acids or alkalis, and melts and decomposes at 246°; its *platinichloride*, $(C_{13}H_{15}ON_3)_2,H_2PtCl_6$, forms microscopic, yellow, glistening prisms, and decomposes above 275°.

6-*Hydroxy*-2-p-*nitrophenyl*-5-*benzyl*-4-*methylpyrimidine*,



$$\mathrm{NO_2\cdot C_6H_4\cdot C}\left<\begin{array}{l}\mathrm{N{=}CMe}\\ \mathrm{N\cdot C(OH)}\end{array}\right>\mathrm{C\cdot CH_2Ph},$$

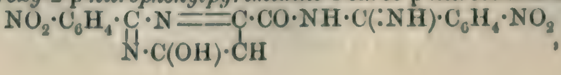
prepared from ethyl benzylacetoacetate, crystallises from dilute acetic acid in long, slender, yellowish needles, melts at 264°, and dissolves readily in acids or alkalis, or in alcohol.

Ethoxalylacetyl-p-*nitrobenzamidine*,

$$NO_2\cdot C_6H_4\cdot C(:NH)\cdot NH\cdot CO\cdot CH_2\cdot CO\cdot CO_2Et,$$

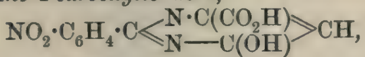
prepared by the action of ethyl oxalylacetate on *p*-nitrobenzamidine, forms small, brown prisms, melts and decomposes at 205°, dissolves readily in acids and alkalis and in pyridine, but is only sparingly soluble in most solvents.

6-*Hydroxy*-2-p-*nitrophenylpyrimidine*-4-*carbo*-p-*nitrobenzamidine*,



$$\begin{array}{l}\mathrm{NO_2\cdot C_6H_4\cdot C\cdot N{=\!=}C\cdot CO\cdot NH\cdot C(:NH)\cdot C_6H_4\cdot NO_2}\\ \qquad\qquad\quad\mathrm{N\cdot C(OH)\cdot CH}\end{array},$$

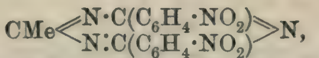
is also produced in this reaction, and is separated from the preceding compound by extracting with water, from which it separates as an oil, and is not readily obtained in crystals. 6-*Hydroxy*-2-p-*nitrophenylpyrimidine*-4-*carboxylic acid*,

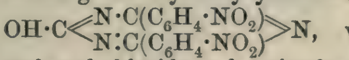


$$NO_2\cdot C_6H_4\cdot C{<}\substack{N\cdot C(CO_2H)\\ N\text{—}C(OH)}{>}CH,$$

prepared by the action of sodium hydroxide on the mixed product from ethyl oxalylacetate and *p*-nitrobenzamidine, separates from acetic acid in minute crystals, melts and decomposes between 261° and 262°, dissolves readily in alcohol or in alkalis, but not in dilute acids; the *basic barium* salt, $C_{11}H_5O_5N_3Ba$, is a crystalline precipitate, and when washed with dilute acetic acid is converted into the normal *barium* salt, $(C_{11}H_6O_5N_3)_2Ba$. A third substance, produced by the interaction of *p*-nitrobenzamidine and ethyl oxalylacetate, is a *compound*, $C_{23}H_{31}O_{12}N_3$, of 1 mol. of the amidine with 2 mols. of the ester, which crystallises from benzene in small prisms, and melts and decomposes at 128°; it is at once decomposed by alkalis.

Acetyl-p-*nitrobenzamide*, $NO_2\cdot C_6H_4\cdot CO\cdot NHAc$, prepared by the action of acetic anhydride on *p*-nitrobenzamidine, forms flat needles, dissolves readily in alcohol and in sodium hydroxide, but only sparingly in acids, and melts at 221°.

Bis-p-*nitrophenylmethylcyanidine*,  $CMe{<}\substack{N\cdot C(C_6H_4\cdot NO_2)\\ N{:}C(C_6H_4\cdot NO_2)}{>}N$, also produced in the preceding interaction, forms flat, yellow needles, is very sparingly soluble in water or alcohol, but readily so in chloroform or acetic acid, and melts at 280°.

Di-p-*nitrobenzamidinecarbamide*, $CO[NH\cdot C(:NH)\cdot C_6H_4\cdot NO_2]_2$, prepared by the action of carbonyl chloride on *p*-nitrobenzamidine, forms flat, yellow, four-sided plates, melts and decomposes at 284°, losing ammonia and forming the hydroxycyanidine. *Bis*-p-*nitrophenylhydroxycyanidine*,  $OH\cdot C{<}\substack{N\cdot C(C_6H_4\cdot NO_2)\\ N{:}C(C_6H_4\cdot NO_2)}{>}N$, which is also formed directly from carbonyl chloride and *p*-nitrobenzamidine, forms yellow needles, does not melt at 305°, is insoluble in most solvents, but dissolves readily in pyridine or in sodium hydroxide; concentrated sodium hydroxide precipitates the crystalline *sodium* salt.

(An attempt to prepare *o*-nitrobenzimino-ether from *o*-nitrobenzonitrile, alcohol, and hydrogen chloride gave only a negative result.)

T. M. L.

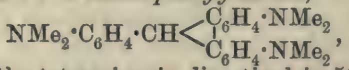
Synthesis of a Phenyldiphenylenemethane Colouring Matter. By ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1901, **132**, 1527—1531).—Hexamethyl-4 : 4′ : 4″ : 2-tetraminotriphenylmethane, when diazotised in dilute hydrochloric or sulphuric acid solution, exchanges its amino-group for hydroxyl, yielding *hexamethyl*-4 : 4′ : 4″-*triamino*-2-*hydroxytriphenylmethane*,

$$NMe_2\cdot C_6H_3(OH)\cdot CH(C_6H_4\cdot NMe_2)_2,$$

crystallising from alcohol in needles and melting at 173°. The hydroxy-base is insoluble in aqueous potassium hydroxide solution, but readily dissolves in an alcoholic solution of the alkali; when oxidised with chloranil, it yields a violet colouring matter.

2-Chlorohexamethyl-4 : 4′ : 4″-triaminotriphenylmethane, produced when the nitrite is added to a solution of the tetramine in concentrated hydrochloric acid, crystallises in colourless needles and melts at 97° ; it is sparingly soluble in hot alcohol, but readily dissolves in benzene or chloroform ; when oxidised with manganese dioxide and acetic acid, it yields a crystalline, blue colouring matter, dyeing wool in a neutral bath.

Hexamethyl-4 : 4′ : 4″-*triaminophenylfluorene*,



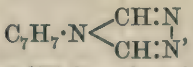
$$NMe_2\cdot C_6H_4\cdot CH{<}\begin{matrix}C_6H_4\cdot NMe_2\\ |\\ C_6H_4\cdot NMe_2\end{matrix},$$

is obtained when the tetramine is diazotised in 50 per cent. sulphuric acid, the yield, however, not exceeding 35 per cent. ; it crystallises from alcohol or benzene in colourless needles and melts at 214°. This compound cannot be obtained by the dehydrating action of sulphuric acid on the hydroxytriamine.

A blue colouring matter is produced when the preceding base is oxidised with lead peroxide ; its *hydrochloride*, $C_{25}H_{28}N_3Cl,2\frac{1}{2}H_2O$, crystallises readily in needles or leaflets somewhat soluble in cold water, but completely precipitated by sodium chloride. When the colouring matter is compared with the crystal violet obtained from the original leuco-base, it is found that the introduction into the molecule of a fluorenic linking results in a change of shade from violet to blue, but produces no other striking modification in the tinctorial properties. The new colouring matter is equally sensitive to acids and alkalis, but less acted on by light ; the affinity for animal fibres decreases, whilst that for vegetable fibres increases ; it does not exhibit fluorescence. G. T. M.

Monosubstituted Derivatives of 1 : 3 : 4-Triazole. By Guido Pellizzari and Matteo Bruzzo (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 414—420. Compare this vol., i, 488).—The following 1 : 3 : 4-triazole derivatives have been obtained by methods analogous to that described for the preparation of the 1-phenyl compound (*loc. cit.*).

1-p-*Tolyl*-1 : 3 : 4-*triazole*, $C_7H_7\cdot N{<}\begin{matrix}CH{:}N\\ |\\ CH{:}N\end{matrix}$, crystallises from water in white leaflets containing $1\frac{1}{2}H_2O$ and melting at 83° ; the water is given off in a desiccator, the anhydrous form thus obtained melting at 116°. It is extremely soluble in alcohol or chloroform, less so in benzene or ether, and slightly in water or light petroleum ; mineral acids readily dissolve it, forming salts from which it is precipitated by potassium hydroxide. Its *platinichloride* forms orange laminæ decomposing at about 215—220°, and on boiling in aqueous solution yields the *compound* $(C_9H_9N_3)_2PtCl_4$ as an insoluble, yellow, amorphous powder. The *picrate* crystallises from alcohol in slender, silky, yellow needles melting at 172°.



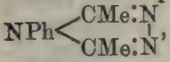
1-o-*Tolyl*-1 : 3 : 4-*triazole*, $C_9H_9N_3$, is deposited from water in prisms melting at 104°, and is very soluble in alcohol or chloroform, moderately so in water or benzene, and to a slight extent in ether. Its platinichloride is unstable, and decomposes even in the cold and in presence of hydrochloric acid, yielding the *compound* $(C_9H_9N_3)_2PtCl_4$, in the form of an insoluble, yellow powder. The *picrate* crystallises from dilute alcohol in slender needles melting at 174°.

1-α-*Naphthyl*-1 : 3 : 4-*triazole*, $C_{12}H_9N_3$, is deposited from benzene in white crystals melting at 120° and is very soluble in chloroform or alcohol, and to a less extent in ether, light petroleum, or water. The platinichloride could not be obtained as it splits up into the *compound*, $(C_{12}H_9N_3)_2PtCl_4$, which is an insoluble, yellow powder. The *picrate* separates from alcohol in small crystals melting at 164°.

1-β-*Naphthyl*-1 : 3 : 4-*triazole*, is deposited from benzene in minute crystals melting at 160° and is soluble in benzene or chloroform, and slightly so in ether or water. The *compound* $(C_{12}H_9N_3)_2PtCl_4$ forms an amorphous, yellow powder and the *picrate* of the base separates from alcohol in very small needles melting at 205°. T. H. P.

Trisubstituted Derivatives of 1 : 3 : 4-Triazole. By GUIDO PELLIZZARI and ANTONIO ALCIATORE (*Atti Real. Accad. Lincei*, 1901, [v], 10, i, 444—452).—Trisubstituted derivatives of 1 : 3 : 4-triazole may be obtained by methods similar to those employed in the preparation of the 1-phenyl compound (this vol., i, 488), using in place of the formyl derivatives of hydrazine and of the primary amine higher acyl derivatives.

In the preparation of 1-*phenyl*-2 : 5-*dimethyl*-1 : 3 : 4-*triazole*,



$NPh<\begin{matrix}CMe{:}N\\ |\\ CMe{:}N\end{matrix}$, the best yield is obtained by the action of diacetylhydrazine on acetanilide; it crystallises from benzene in silky, white needles melting at 237°, which dissolve readily in alcohol, chloroform, or water, and to a slight extent in ether or light petroleum; it is soluble in mineral acids, from which it is precipitated by potassium hydroxide solution, and volatilises when heated. The *platinichloride* separates from hydrochloric acid in tufts of needles which melt and decompose at 256—257°. The *picrate* is deposited from water or alcohol in long, yellow crystals melting at 175°.

1-o-*Tolyl*-2 : 5-*dimethyl*-1 : 3 : 4-*triazole*, $C_{11}H_{13}N_3$, separates from benzene in white crystals which melt at 168° and dissolve readily in water, alcohol, or chloroform, and to a less extent in ether or light petroleum. Its *platinichloride* crystallises from hydrochloric acid in tufts of needles melting and decomposing at 244—245° and when boiled in dilute aqueous solution yields the *compound* $(C_{11}H_{13}N_3)_2PtCl_4$ as a pale-yellow, amorphous, insoluble powder decomposing at about 255°. The *picrate* separates from alcohol in acicular crystals melting at 164°.

1-p-*Tolyl*-2 : 5-*dimethyl*-1 : 3 : 4-*triazole* crystallises from benzene in minute needles melting at 228° and dissolves readily in water, alcohol, or chloroform, and slightly in light petroleum. Its platinichloride could not be obtained crystalline, but on boiling with water yields the *compound* $(C_{11}H_{13}N_3)_2PtCl_4$ as a yellow, insoluble powder melting and decomposing at 250—254°. The *picrate* separates from alcohol in slender, yellow crystals melting at 158°.

1 : 2 : 5-*Triphenyl*-1 : 3 : 4-*triazole*, $C_{20}H_{15}N_3$, prepared by the interaction either of dibenzoylhydrazine and benzanilide or of dibenzoylhydrazine and aniline, crystallises from alcohol in slender, white

needles melting at 304—305° and dissolves slightly in benzene but is insoluble in water, ether, or light petroleum; it has weak basic properties and forms a *hydrochloride* separating in white crystals.

T. H. P.

Constitution of the Hydroxyazo-compounds. By WILLIAM McPHERSON and HERBERT C. GORE (*Amer. Chem. J.*, 1901, **25**, 485—496. Compare Abstr., 1900, i, 123).—*a-Benzoyl-β-acetyl-a-naphthylhydrazine*, obtained by the action of benzoyl chloride on β-acetylnaphthylhydrazine, separates from alcohol in large crystals and melts at 184°; it is converted by dilute sulphuric acid into *a-benzoyl-a-naphthylhydrazine*, $C_{10}H_7\cdot NBz\cdot NH_2$, which crystallises from alcohol in truncated pyramids, melts at 120·5°, and dissolves readily in alcohol or benzene. On the addition of light petroleum to a benzene solution of the last-mentioned compound, feathery crystals melting at 98° are deposited, but when these are gently heated the melting point gradually rises to 120·5°. The following hydrazones were prepared by the interaction of quinones with a-benzoyl-a-naphthylhydrazine.

Quinonebenzoyl-a-naphthylhydrazone, $O{:}C_6H_4{:}N\cdot NBz\cdot C_{10}H_7$, crystallises from light petroleum in plates, melts at 113·5°, and is very soluble in benzene, alcohol, ether, or chloroform; both this substance and the isomeric benzoyl-a-naphthaleneazophenol yield a-naphthaleneazophenol on hydrolysis. *a-Naphthaleneazophenol* may be readily prepared by the action of phenol on a-naphthyldiazonium chloride; it melts at 136°, crystallises from alcohol in brown needles, from benzene in yellow needles, and from light petroleum in brown plates which, when heated to 130°, suddenly become red; this red modification separates from a solution in light petroleum in reddish, silky needles. The *benzoate*, $OBz\cdot C_6H_4\cdot N{:}N\cdot C_{10}H_7$, crystallises in needles, melts at 120°, and dissolves readily in chloroform or benzene.

Toluoquinonebenzoyl-a-naphthylhydrazone, $O{:}C_6H_3Me{:}N\cdot NBz\cdot C_{10}H_7$, forms prismatic crystals and melts at 166°; this compound, like the isomeric benzoyl-a-naphthaleneazo-*o*-cresol, yields a-naphthaleneazo-*o*-cresol on hydrolysis. *a-Naphthaleneazo-*o*-cresol* may be obtained by the interaction of a-naphthyldiazonium chloride and *o*-cresol; it crystallises from benzene in reddish-yellow needles, melts at 154·5°, and is readily soluble in alcohol or benzene. Its *benzoate* crystallises from light petroleum in long, thin, flat needles and melts at 120°.

Thymoquinonebenzoyl-a-naphthylhydrazone,

$$O{:}C_6H_2MePr^{\beta}{:}N\cdot NBz\cdot C_{10}H_7,$$

crystallises from alcohol in rhombohedra, melts at 151·5°, and furnishes a-naphthaleneazothymol on hydrolysis. *a-Naphthaleneazothymol*, prepared by the action of thymol on a-naphthyldiazonium chloride, separates from a mixture of benzene and light petroleum in monoclinic crystals, melts at 117·5°, and is soluble in ether, benzene, or alcohol. Its *benzoate* crystallises in needles, dissolves readily in ether or benzene, and melts at 173·5°.

E. G.

Hydroxyazoaldehydes. By WALTHER BORSCHE and C. E. BOLSER (*Ber.*, 1901, **34**, 2094—2104. Compare Abstr., 1900, i, 419).—*p*-Hydroxybenzaldehyde does not react with a diazo-solution prepared from aniline, whilst *m*-hydroxybenzaldehyde undergoes a vigorous reaction accompanied by evolution of nitrogen, but does not yield a colouring matter. The semicarbazones of the isomeric hydroxybenzaldehydes have not previously been described. The *meta*-compound crystallises in compact, yellow needles melting at 198°; the *para*-compound is a yellowish, crystalline powder melting at 223—225°, and the *ortho*-compound crystallises in faintly yellow needles melting at 231—232°. Resorcylaldehyde, $C_6H_3(OH)_2\cdot CHO$ [2 : 4 : 1], readily reacts with diazobenzene chloride, but the product is very unstable in alkaline solution. *Benzeneazoresorcylaldehyde* is therefore best prepared in alcoholic solution, but can only be recrystallised in small quantities. The *phenylhydrazone*, $Ph\cdot N_2\cdot C_6H_2(OH)_2\cdot CH\!:\!N\cdot NHPh$, crystallises in lustrous, blackish-brown needles which melt and decompose at 217°.

o-Cresolaldehyde (2-hydroxy-*m*-tolualdehyde) reacts with diazobenzene chloride to form 5-*benzeneazo-2-hydroxy*-m-*tolualdehyde*,

$$Ph\cdot N_2\cdot C_6H_2Me(OH)\cdot COH,$$

which crystallises in yellowish-red needles melting at 76°. The same compound can be prepared from benzeneazo-*o*-cresol by Tiemann and Reimer's reaction. The *anilide* crystallises in brownish-yellow plates melting at 77—78°; the *phenylhydrazone* forms yellowish-red plates melting at 147—148°; and the *a-naphthylimine* crystallises in large plates which have a golden lustre and melt at 158—160°. A diazo-solution prepared from sulphanilic acid also reacts with this aldehyde, forming *sodium* 5-p-*sulphobenzeneazo-2-hydroxy*-m-*tolualdehyde*, $SO_3Na\cdot C_6H_4\cdot N_2\cdot C_6H_2Me(OH)\cdot CHO,2H_2O$, which crystallises in yellowish plates. On treatment with bromine, it yields 5-*bromo-2-hydroxy*-m-*tolualdehyde*, $OH\cdot C_6H_2BrMe\cdot CHO$, which is also formed by the direct action of bromine on *o*-hydroxytolualdehyde, and crystallises in silky needles melting at 78°. The *phenylhydrazone* crystallises in yellowish plates and melts at 137—138°. 5-*Bromo-2-hydroxy*-m-*toluic acid*, $OH\cdot C_6H_2BrMe\cdot CO_2H$, is formed by the direct bromination of 2-hydroxy-*m*-toluic acid, and crystallises in white needles melting at 231—232°; the *barium* salt is moderately soluble in water. 2-*Hydroxy-1-methyl-3-ketophenylpropenyl-5-benzeneazobenzene*, $Ph\cdot N_2\cdot C_6H_2Me(OH)\cdot CH\!:\!CH\cdot COPh$, is formed by the condensation of benzeneazohydroxytolualdehyde with acetophenone, and forms a reddish-yellow, crystalline powder which melts and decomposes at 180—181°. The corresponding *sodium sulphonate* is prepared in a similar manner from sulphobenzeneazohydroxytolualdehyde, and forms reddish-yellow crystals. All attempts to obtain the corresponding saturated compounds have hitherto proved unavailing. 3-Hydroxy-*p*-tolualdehyde readily reacts with diazobenzene chloride to form 6-*benzeneazo-3-hydroxy*-p-*tolualdehyde*, which melts at 143—144°. The *phenylhydrazone* crystallises in lustrous plates melting at 123—125°. 6-Hydroxy-*m*-tolualdehyde and 4-hydroxy-*m*-tolualdehyde do not react with diazobenzene chloride.
A. H.

Benzylazide [Benzylazoimide]. By THEODOR CURTIUS and AUGUST DARAPSKY (*J. pr. Chem.*, 1901, ii, 63, 428—444. Compare Abstr., 1900, i, 698, 699).—Benzylazoimide can be obtained, not only from nitrosobenzylhydrazine (*loc. cit.*), but also by the interaction of silver-azoimide and benzyl iodide. The stability towards alkalis cannot therefore be accounted for by supposing that benzylazoimide has not the constitution of an ester of azoimide. By the action of mineral acids (sulphuric and hydrochloric), the azoimide undergoes a series of decompositions, which are thus represented by the authors:

(1) $CH_2Ph{\cdot}N_3 = CH_2Ph{\cdot}N< + N_2$. The group $CH_2Ph{\cdot}N<$ is then partly transformed either into $CHPh{\colon}NH$, an iminoaldehyde which with water gives benzaldehyde and ammonia; or (2) into $CH_2{\colon}NPh$, a methyleneamine, which then with water yields aniline and formaldehyde. (3) The azoimide partly also reacts with water, forming benzylamine and nitrous oxide; $CH_2Ph{\cdot}N_3 + H_2O = CH_2Ph{\cdot}NH_2 + N_2O$. (4) Lastly, azoimide is evolved probably owing to hydrolysis of benzylazoimide. The authors point out that the formation of aniline virtually represents the replacement of CH_3 by NH_2.

In carrying out the experiments, benzaldehyde was separated by distilling in steam from the acid product of the reaction. After making alkaline, the ammonia, aniline, and benzylamine are distilled over in steam, and the last two separated by passing carbon dioxide into their ethereal solution, when benzylamine carbonate is precipitated. When the acid liquor is neutralised, a yellow *base* is precipitated which is insoluble in all solvents except chloroform; it decomposes at 250°, and is readily soluble in acids, forming a red solution; its diazo-derivative condenses with resorcinol, yielding a red azo-colouring matter. This base is also obtained by the action of sulphuric acid on a mixture of aniline and paraformaldehyde, and on anhydroformaldehydeaniline. Hydrochloric acid differs from sulphuric acid in its action on benzylazoimide in producing less benzaldehyde, and more benzylamine and yellow base.

Details are given in the paper of the preparation of the azoimide from benzylhydrazine, the *dihydrochloride* of which crystallises in short thick prisms melting at 145° with evolution of gas. Boiling with water, alcohol, or alcoholic potash are without effect on benzylazoimide, and it is not oxidised by prolonged boiling with aqueous lead nitrate.

K. J. P. O.

Auto-oxidation of Hydrazobenzene. By Wilhelm Manchot and Johannes Herzog (*Annalen*, 1901, **316**, 331—332. Compare this vol., i, 565; ii, 93).—When hydrazobenzene, dissolved in an alcoholic solution of sodium ethoxide, is shaken with oxygen, the amount of this gas absorbed corresponds with the equation $N_2H_2Ph_2 + O_2 = H_2O_2 + N_2Ph_2$. The hydrogen peroxide produced interacts with the sodium ethoxide yielding sodium peroxide, which, under these conditions, is precipitated; in this way, any secondary change due to the oxidising action of the peroxide on the organic compound is entirely prevented.

G. T. M.

Hydrazo-compounds. Reduction Products of *o*- and *p*-Nitrodiphenyl and the Products of the Transformation of Hydrazodiphenyls. By Georg Friebel and Berthold Rassow (*J. pr. Chem.*, 1901, [ii], **63**, 444—465).—The compound described by Zimmermann (Abstr., 1881, 175) as *p*-hydrazodiphenyl is shown to be slightly impure *p*-azodiphenyl (m. p. 249°). p-*Hydrazodiphenyl*, $N_2H_2(C_6H_4Ph)_2$, is prepared by the reduction of *p*-nitrodiphenyl by alcoholic potassium hydroxide and zinc dust, and is purified by recrystallisation from ether, every precaution being taken to avoid contact with the air, which immediately oxidises it to the azo-compound; the base forms colourless leaflets melting at 167—169°. By concentrated hydrochloric acid it is converted into *p*-aminodiphenyl (m. p. 53°). The *hydrochloride* of the latter forms leaflets, the *sulphate* needles, and the *platinichloride* golden-yellow leaflets (compare Hübner, *Annalen*, 1881, **209**, 342). The *diacetyl* derivative crystallises in white needles melting at 120°. The *benzoyl* derivative of *p*-hydroxydiphenyl crystallises in colourless needles melting at 147—148°.

o-*Azoxydiphenyl*, prepared by reduction of *o*-nitrodiphenyl, forms crystals melting at 157—158°.

o-*Hydrazodiphenyl*, prepared by reduction of the last-mentioned compound, crystallises in colourless needles melting at 182°, which are only slowly oxidised by the air.

3 : 3′-*Diphenylbenzidine* is formed on heating the hydrazo-compound at 100° with concentrated hydrochloric acid, and crystallises in large plates melting at 151—152°. The *dihydrochloride* crystallises in needles, little soluble in water, and the *platinichloride* in yellow leaflets. The *diacetate*, formed when the base is boiled with acetic anhydride, melts at 224—227°; the *diacetyl* derivative, prepared by heating the base at 100° with thioacetic acid, crystallises in colourless needles melting at 245—246°. With carbon disulphide, the base gives an insoluble, crystalline *compound* melting at 195—196°.

o-*Azodiphenyl*, prepared by oxidising *o*-hydrazodiphenyl with ferric chloride, crystallises in reddish-purple needles melting at 144·5°.

K. J. P. O.

Products of the Digestion of Albumin. III. The so called Amphopeptone. By Sigmund Fränkel and Leo Langstein (*Monatsh.*, 1901, **22**, 335—345. Compare Abstr., 1899, i, 396).—Recent work has shown that Kühne's amphopeptone is a mixture of two very different substances. The authors find that on treatment with alcohol amphopeptone partly dissolves. The soluble fraction yields only the biuret reaction, gives a precipitate with bromine or iodine in potassium iodide, and contains sulphur. On benzoylating by Schotten-Baumann's method and extracting with ether, a soluble benzoyl derivative of a compound free from sulphur goes into solution, whilst a small quantity of an insoluble substance containing sulphur remains. The soluble benzoyl compound gives only the biuret reaction, and is probably the derivative of a protamine.

The fraction insoluble in alcohol consists of two parts, a peptone which gives Millon's, the biuret, and the xanthoproteic reactions, and a substance which gives Molisch's reaction, and is identical with the carbohydrate complex of albumin (albamin).

In the experiments, coagulated albumin, prepared from egg-albumin free from globulin, was digested with pure pepsin in the presence of hydrochloric acid. The peptone was isolated in some cases by saturating the fluid products of digestion with ammonium sulphate at 100°, filtering, and adding twice the volume of alcohol; the alcoholic extract was evaporated and then poured into absolute alcohol, when the fraction insoluble in this medium separates. Addition of ether precipitates from the alcohol the soluble fraction, which gives only the biuret reaction. In other cases, the fluid products of digestion were evaporated under reduced pressure, and the residual syrup extracted with alcohol; from the solution, ether precipitated the soluble fraction.

From Witte's peptone, a soluble fraction was obtained in a similar manner. K. J. P. O.

Chemical Nature of Trypsin. By P. A. Levene (*Amer. J. Physiol.*, 1901, **5**, 298—300).—The experiments recorded do not justify the conclusion that trypsin is a nucleo-compound. Only those solutions are active which give the biuret test; this would seem to indicate that trypsin is of proteid nature. However, in some cases the biuret test was scarcely perceptible, and yet the solution of self-digested trypsin still contained the active ferment. W. D. H.

Action of Trypsin on Fibrin. By Horace M. Vernon (*J. Physiol.*, 1901, **26**, 405—426).—The method suggested for the estimation of the tryptic value of a pancreatic extract is as follows. About 1·8 c.c. of finely chopped fibrin are introduced into a 10 c.c. graduated tube filled with distilled water. This is centrifugalised for 2 minutes. The volume of fibrin, now reduced to about 1 c.c., is read off. Five c.c. of the water are then replaced by 2 per cent. solution of sodium carbonate, and the mixture kept at 38° for an hour; the fibrin swells up. Six c.c. of liquid are then withdrawn, and replaced by water containing 1 c.c. of the extract to be tested. After a given time, centrifugalisation is again performed for 1 minute, and the volume of the remaining fibrin read off. The time is noted when about 80 per cent. of the fibrin has disappeared; this is corrected to exactly 80 per cent., and so tables of relative tryptic value can be constructed. Each estimation takes about a quarter of an hour. Sodium carbonate rapidly destroys trypsin, and trypsin appears to consist of a series of ferments with different degrees of stability. Allowing for the ferment destroyed during an experiment, the rate of digestion varies as the square root of the quantity of ferment present (Schütz's law).

W. D. H.

Constitution of Organo-mercury Compounds of Benzoic Acid. By Leone Pesci (*Atti Real. Accad. Lincei*, 1901, [v], **10**, i, 362—363).—The hydroxymercuribenzoic anhydride previously described (see Abstr., 1900, i, 546) by the author is also produced by the action of mercuric acetate on phthalic acid, so that in this anhydride, and also in the corresponding acid and its derivatives, the mercury must occupy the ortho-position to the carboxyl residue, and not the para-position, as was previously supposed (*loc cit.*). T. H. P.

Organic Chemistry.

Action of Nitric Acid on Secondary Alcohols. By GIACOMO PONZIO (*Gazzetta*, 1901, **31**, i, 401—406).—The action of nitric acid on secondary alcohols gives rise to α-diketones as principal product, together with dinitro-paraffins. Methylethylcarbinol yields, with nitric acid, dimethyl diketone and dinitroethane; diethylcarbinol gives methyl ethyl diketone and dinitroethane; methylbutylcarbinol, methyl propyl diketone and dinitrobutane, whilst methylhexylcarbinol and nitric acid yield methyl amyl diketone and dinitrohexane. The statement found in some text-books that the action of nitric acid on diethylcarbinol or on diethyl ketone yields dinitropropane is inaccurate, as the author's results show. T. H. P.

Preparation of Dimethyl Sulphate. By M. BENNETT BLACKLER (*Chem. News*, 1901, **83**, 303—304).—The preparation of dimethyl sulphate from methyl alcohol and sulphuric acid is best carried out in two stages. Dimethyl ether is first prepared and is absorbed in sulphuric acid kept at 160°. This solution, when distilled above 160°, gives a 21 per cent. yield of dimethyl sulphate. R. H. P.

Ethylene Derivatives. By LOUIS HENRY (*Rec. trav. Chim.*, 1901, **20**, 243—254).—Ethylene diacetate readily absorbs hydrogen bromide, yielding acetic acid and bromoethyl acetate, $CH_2Br\cdot CH_2\cdot OAc$ (Demole, this Journ., 1874, 783). The latter boils at 162—163°, has a sp. gr. 1·524 at 9°, and solidifies to colourless needles melting at −13·8°. The bromine is readily replaceable, but not quite so readily as in the isomeric ethyl bromoacetate.

Iodoethyl acetate, $CH_2I\cdot CH_2\cdot OAc$, obtained by the action of sodium iodide on the bromo-derivative, is a colourless liquid with a pleasant odour, boils at 110° under 60 mm. pressure, and has a sp. gr. 2·441 at 20°. Ethylene monobromohydrin is formed when the bromo-derivative is boiled with water, ethyl alcohol, or best of all with methyl alcohol.

Attempts to prepare bromoethyl acetate by the action of potassium acetate (1 mol.) and a little acetic acid on ethylene dibromide proved fruitless, the product always formed being the diacetate.

Ethylene iodohydrin is readily obtained by the action of sodium iodide on bromoethyl acetate in the presence of methyl alcohol.

J. J. S.

Mixed Glycerides in Natural Fats. By D. HOLDE and M. STANGE (*Ber.*, 1901, **34**, 2402—2408).—The authors have investigated the solid constituents of olive oil, which have previously been regarded as a mixture of triolein, tripalmitin, and tristearin. On cooling an ethereal solution of olive oil to −40 or −45°, the solid glycerides separated as a white, crystalline precipitate, which was freed from liquid oil by repeated recrystallisation from ether at a low temperature, and finally from alcohol and ether at the ordinary temperature.

By this means, 5—10 grams of pure solid glyceride were isolated from 400—700 grams of olive oil. The glyceride crystallises from dilute alcohol in soft needles, melting at 29—31°, and having a sp. gr. 0·9948 in the molten state and a mol. wt. 857—860. Determinations of the saponification number, iodine number, total fatty acid, and proportion of glycerol all lead to the conclusion that the glyceride is an oleodimargarin, $C_3H_5(C_{17}H_{33}O_2)_2\cdot C_{18}H_{33}O_2$.

The glyceride was hydrolysed by a cold alcoholic solution of lead acetate, and the lead salts of the fatty acids separated by extraction with ether. The proportion of solid to liquid acid was found 2·2 : 1, instead of 1·9 : 1, required by the above formula. The solid fatty acid melted at 59—61°, was saturated, had a mol. wt. 265·4, and in other ways resembled margaric acid, whilst the mol. wt., iodine number, &c., of the liquid acid were those of oleic acid.

K. J. P. O.

Sorbic Acid. By OSCAR DOEBNER and A. WOLFF (*Ber.*, 1901, **34**, 2221—2223. Compare Abstr., 1900, i, 526).—*Sorbyl chloride*, $C_5H_7\cdot COCl$, prepared by the action of phosphorus pentachloride on the acid, is a colourless liquid which has a penetrating odour, and boils at 78° under 15 mm. pressure. *Methyl sorbate*, $C_5H_7\cdot CO_2Me$, prepared from the alcohol and sorbyl chloride, is a colourless liquid which boils at 174° and freezes at 5°. Ethyl sorbate is best prepared from the chloride, and has already been described by Hofmann (*Annalen*, 1859, **110**, 137). *Sorbamide*, $C_5H_7\cdot CO\cdot NH_2$, crystallises in slender needles melting at 168°. *Sorbanilide*, $C_5H_7\cdot CO\cdot NHPh$, crystallises in lustrous scales melting at 153°. *Sorbonitrile*, $C_5H_7\cdot CN$, is a colourless oil and boils at 72° under 20 mm. pressure. The *ketone*, $C_5H_7\cdot COEt$, prepared by Freund's reaction with zinc ethyl, is a light yellow coloured oil which boils at 90—95° under 26 mm. pressure.

A. H.

Cineolic Acid. III. By HANS RUPE and MAX RONUS (*Ber.*, 1901, **34**, 2191—2206. See Abstr., 1900, i, 371, and this vol., i, 119).—The acid obtained (*loc. cit.*) by the action of sulphuric acid on cineolic acid is stereoisomeric with the cinenic acid previously described (*loc. cit.*); it is now called β-cinenic acid to distinguish it from the latter, which is called α-cinenic acid; this is probably an instance of *cis*- and *trans*-isomerism.

α-Cinenic acid, when treated with hydrogen bromide in glacial acetic acid solution, yields *δ-bromo-α-hydroxy*iso*propylhexoic acid*, $CHMeBr\cdot CH_2\cdot CH_2\cdot CH(CO_2H)\cdot CMe_2\cdot OH$, which crystallises in stellate needles, melts at 97—98°, and, when treated with alcoholic potash, yields the α-hydroxy*iso*propyl-γ-hexenoic acid previously described, and, when treated with water, cinogenic acid.

Cinogenic acid (*δ-hydroxy-α-hydroxy*iso*propylhexoic acid*),

$$OH\cdot CHMe\cdot CH_2\cdot CH_2\cdot CH(CO_2H)\cdot CMe_2OH,$$

which forms the portion insoluble in ether of the products of the action of water under pressure on cineolic acid, crystallises in glistening, six-sided tablets, melts at 104·5—105°, and forms easily soluble salts, except the *magnesium* and *cobalt* salts, which both crystallise with $2H_2O$;

when distilled under reduced pressure, or heated with water under pressure, it yields *α*-cinenic acid.

β-Cinenic acid is a clear oil boiling at 122—123° under 10 mm. pressure, has a conductivity λ_{1024}—λ_{32} 11·44 at 20°, and a refractive index n_D 1·4486; it forms a characteristic *calcium* salt, which crystallises in stellate needles, and has a solubility of 1 part in 74·4 parts of water at 17°, the corresponding salt of *α*-cinenic acid being amorphous, and having a solubility of 1 part in 460 parts of water at 17°. *α*-Cinenic acid can be converted into the *β*-isomeride by heating with dilute sulphuric acid under pressure, and the latter can also be converted into cinogenic acid by the method described above. R. H. P.

Product of Nitration of Ethyl Acetoacetate. By LOUIS BOUVEAULT and A. BONGERT (*Compt. rend.*, 1901, **133**, 103—104).—By the nitration of ethyl acetoacetate, the authors have obtained a substance, $C_2N_2O_2(CO_2Et)_2$, which is an oil, isomeric with the substance obtained by Scholl (this vol., i, 359) by the action of silver nitrate on ethyl bromoacetate, and called by him ethyl bisanhydronitroacetate. The diamide prepared by Scholl melted and exploded at 121°, whilst the isomeric *amide* obtained by the authors melted at 253°. Scholl prepared a number of crystalline diamides from his ester, and both primary and secondary amines; with primary amines, on the other hand, the authors obtained only oily products, whilst with secondary amines a more profound reaction took place.

When dimethylamine is passed into an ethereal solution of the ester, heat is developed, and the solution becomes of a bright red colour. A red oil separates and soon solidifies. This *substance*, $C_7H_{14}O_3N_4$, forms red crystals, melting at 129°, and is the dimethylamine salt of an *acid*, $C_5H_7O_3N_3$, which separates in crystals melting and decomposing at 182°. From the ethereal mother liquor of the dimethylamine salt, ethyl alcohol and dimethylurethane were obtained. The reaction between the ester and dimethylamine may be thus represented: $3NHMe_2 + C_2O_2N_2(CO_2Et)_2 = C_2H_6O + NMe_2{\cdot}CO_2Et + C_5H_7O_3N_3{,}NHMe_2$. To the acid, the formula $C_2HO_2N_2{\cdot}CO{\cdot}NMe_2$ is given.

With diethylamine, the diethylamine salt of an *acid*,

$$C_2HO_2N_2{\cdot}CO{\cdot}NEt_2,$$

is obtained; the acid forms ruby-red crystals, melting and decomposing at 143°; the *salt*, $C_7H_{11}O_3N_3{\cdot}NHEt_2$, crystallises in orange scales melting at 112°. The urethane was not isolated.

With piperidine, the ester gave alcohol, piperidylurethane, and the piperidine salt of the corresponding acid. The *acid*,

$$C_2HO_2N_2{\cdot}CO{\cdot}C_5NH_{10},$$

forms orange-red crystals melting and decomposing at 162°; the *piperidine* salt, orange crystals melting and decomposing at 148°. *Piperidylurethane*, $C_5H_{10}N{\cdot}CO_2Et$, is a colourless liquid boiling at 103° under 20 mm. pressure. K. J. P. O.

Chromium Oxalate. By GRÉGOIRE N. WYROUBOFF (*Chem. Centr.*, 1901, i, 1362—1363; from *Bull. Soc. franç. Min.*, **24**, 86—92).—An amorphous chromium oxalate, soluble in water in all proportions, is obtained by reducing chromic acid in presence of oxalic acid, or by dissolving chromium oxide in oxalic acid. When the solution is evaporated at the ordinary temperature by exposure to the air, it leaves a violet liquid, but when evaporated on the water-bath, a green liquid remains, which, on treatment with water, becomes violet. The normal chromium oxalate, $Cr_2O_3,3C_2O_3,25H_2O$, forms monoclinic, violet crystals, and is obtained by mixing a solution of an alkali oxalate (3 mols.) with a freshly prepared 10—15 per cent. solution of a chromium salt (1 mol.). From concentrated solutions of chromium salts, an oxalate containing $13H_2O$ separates in grey needles, which in the dry state may be kept without change, but forms very unstable solutions. The hydrate containing $25H_2O$ loses $12H_2O$ on exposure to the air for a long time, or on boiling with alcohol for a few minutes. Both hydrates are completely insoluble in water; the last mol. of water cannot be removed without partial decomposition. The hydrates, with $4H_2O$ and $1H_2O$ respectively, are crystalline substances soluble in water or alcohol. They are to be regarded as abnormal salts of the composition $Cr_2O_2(OH)_2,C_2O_4H_2$ and $Cr_2O_2(OH)_2,3C_2O_3$ respectively, whilst the normal oxalates contain more water, and have the composition $Cr_2(OH)_6,3C_2O_4H_2,19H_2O$ and $Cr_2(OH)_6,3C_2O_4H_2,7H_2O$ respectively.

When a crystalline chromium salt (1 mol.) is treated with cold sodium hydroxide or potassium hydroxide solution (6 mols.), a pale green oxide is formed, which, after drying over sulphuric acid, has the composition $Cr_2O_3,8H_2O$ or $Cr_2(OH)_6,5H_2O$. It loses $2H_2O$ at 110° without alteration of colour, and at a considerably higher temperature forms the hydrate $Cr_2O_2(OH)_2,H_2O$; the last mol. of water is given off only at a red heat. The abnormal oxalate does not give a precipitate with cold sodium hydroxide or potassium hydroxide solutions, but only after boiling for some minutes; the precipitated oxide,

$$Cr_2(OH)_6,3H_2O,$$

loses $2H_2O$ at 110°. E. W. W.

Influence of Molybdic Acid and Molybdates on the Specific Rotation of Malates. By HERRMANN ITZIG (*Ber.*, 1901, 34, 2391—2401. Compare Gernez, Abstr., 1889, 1147; 1890, 744; 1891, 291).—Saturated solutions of normal sodium or potassium *l*-malate readily dissolve molybdic acid. The composition of the dissolved sodium salt (dimolybdylmalate) is represented by the formula $Na_2O,2MoO_3,C_4H_4O_4$, and has $[\alpha]_D$ +743° at 17°, whilst the potassium salt has $[\alpha]_D$ +731° at 18°. Solutions of molybdylmalates, $M'_2O,MoO_3,C_4H_4O_4$, are obtained by dissolving molybdic acid (1 mol.) in solutions of malates (1 mol.); the sodium salt has $[\alpha]_D$ +136° at 17°, and the potassium salt $[\alpha]_D$ +153·9° at 18°. Molybdylmalates, $(M'_2O,H_2O,C_4H_4O_4)_2,MoO_3$, have been prepared as crystalline compounds by Henderson (Trans., 1899, 75, 542). The ammonium salt has $[\alpha]_D$ −87·2° at 17°. In the case of all the above salts, $[\alpha]_D$ decreases with dilution.

The author has investigated the action of molybdic acid and sodium molybdate and paramolybdate on the specific rotation of *l*-malic acid and its normal and acid sodium and ammonium salts. In all cases, addition of the molybdenum compound initially increases the lævorotation of the malic acid or its salt to a maximum. As the proportion of the former increases, the lævorotation begins to decrease, and finally passes into a dextrorotation, which in some cases becomes very great.

K. J. P. O.

Brown-Coal Tar. By THEODOR ROSENTHAL (*Zeit. angew. Chem.*, 1901, **14**, 665—667. Compare Abstr., 1892, 1075, and 1895, i, 258). —The following substances have been found in the products of destructive distillation of brown coal:—(*a*) Saturated and unsaturated aldehydes, the only one isolated in a pure state, so far, is acetaldehyde. (*b*) Ketones, both acetone and methyl ethyl ketone have been isolated. (*c*) Methyl alcohol. (*d*) Acetonitrile.

J. J. S.

Action of Acid Chlorides on Methanal [Paraformaldehyde]. By LOUIS HENRY (*Compt. rend.*, 1901, **133**, 96—98. Compare Abstr., 1900, i, 537).—Chloromethyl acetate is formed in the reaction of acetyl chloride on paraformaldehyde. When a fragment of fused zinc chloride is present (compare Descudé, this vol., i, 357), the reaction takes place more easily. By a similar method, *chloromethyl benzoate*, $C_6H_5\cdot CO_2\cdot CH_2Cl$, is obtained from benzoyl chloride and paraformaldehyde; the ester is an oil which, at 200°, decomposes into its constituents.

K. J. P. O.

Syntheses of Aldehydes of the Acetylene Series. By CHARLES MOUREU and RAYMOND DELANGE (*Compt. rend.*, 1901, **133**, 105—107. Compare this vol., i, 442).—On adding the sodium derivatives (1 mol.) of the acetylene hydrocarbons, suspended in absolute ether at 0° to ethyl formate (2 mols.), an immediate reaction takes place and the liquid becomes yellow. After 6 hours' standing at 0° the major part of the sodium derivative has disappeared. Ice is added, and the ethereal layer separated; after evaporation of the ether, the residue, which consists chiefly of an aldehyde of the acetylene series, is distilled under reduced pressure (yield from 15—18 per cent.).

Œnanthylidene [heptinene] yields *amylpropiolaldehyde*,

$$CH_2Me\cdot[CH_2]_3\cdot C⋮C\cdot CHO,$$

a colourless liquid, distilling at 89° under 26 mm. and at 185—187° under atmospheric pressure.

Phenylacetylene yields phenylpropiolaldehyde (Claisen, Abstr., 1898, i, 422, 423), which boils at 127—128° under 28 mm. pressure, and has a sp. gr. 1·0791 at 0°. The absence of the typical hydrogen atom of the acetylene hydrocarbons prevents the formation of metallic derivatives. With boiling aqueous solutions of alkalis, these aldehydes decompose, yielding the acetylene hydrocarbon and a formate. From amylpropiolaldehyde is also formed some methyl amyl ketone, and traces of hexoic acid.

The authors express the opinion that initially an additive product of the sodium acetylide and ethyl formate is formed; with water, this decomposes partly into an aldehyde, alcohol, and sodium hydroxide, and partly into the original acetylene hydrocarbon, alcohol, and sodium formate.

K. J. P. O.

Action of Hydrogen Sulphide on Acetylacetone. By F. LETEUR (*Compt. rend.*, 1901, **133**, 48—49).—Hydrogen sulphide has no action on acetylacetone, alone or in presence of acetic acid and sodium acetate, but in presence of concentrated hydrochloric acid a polymeride of dithioacetylacetone, $(C_5H_8S_2)_2$, is obtained. It is volatile in steam, and forms long channelled, acicular, triclinic prisms which melt at 162—163·5°, and sublime at a lower temperature. It is soluble in most organic solvents and in hot alcohol, but is only slightly so in cold alcohol and insoluble in water. C. H. B.

Cellulose. By Richard Wolffenstein and G. Bumcke (*Ber.*, 1901, **34**, 2415—2417. Compare Abstr., 1899, i, 852; Tollens, this vol., i, 453).—A controversial paper. W. A. D.

Dextrorotatory *sec.*Butylamine. By Johannes Gadamer (*Arch. Pharm.*, 1901, **239**, 283—294. Compare Abstr., 1899, i, 534).—The *sec.*butylamine, prepared from the dextrorotatory *sec.*butylthiocarbamide (from *Cochlearia officinalis*) (*loc. cit.*), is now shown to be dextrorotatory and not inactive ($[\alpha]_D$ +6·42° at 15·5°). A list is given of the specific and molecular rotations of *sec.*butyl- carbamide, -thiocarbamide, and -thiocarbimide derivatives; and the influence of the different groups attached to the asymmetric carbon atom on the magnitude of the specific rotation is discussed.

*sec.*Butylamine is prepared from the essential oil of *Cochlearia officinalis* by reduction with zinc dust and sulphuric acid in dilute alcoholic solution; it has a sp. gr. 0·7393. The *hydrochloride* is very hygroscopic, and in aqueous solution has $[\alpha]_D$ −2·05° at 20°; the *platinichloride* forms dark, yellowish-red prisms, melting and decomposing at 204—210°. *sec.*Butylthiocarbimide is obtained by the action of carbon disulphide on the amine; addition of mercuric chloride to the product precipitates the mercuric salt of butylthiocarbamic acid, which decomposes at the ordinary temperature into mercuric sulphide and butylthiocarbimide.

d-d-*Dibutylcarbamide*, prepared by the action of mercuric oxide on *d-d*-dibutylthiocarbamide, crystallises in needles which have $[\alpha]_D$ +39·71° at 20° when in solution in absolute alcohol.

K. J. P. O.

Derivatives of Ethylene Ethyl Alcohol and Ethylene Acetic Acid. By Louis Henry [and Paul Dalle] (*Rec. trav. Chim.*, 1901, **20**, 255—258).—*Ethylene ethylamine* [*trimethylenecarbinylamine*],

$\left.\begin{matrix}CH_2\\|\\CH_2\end{matrix}\right>CH\cdot CH_2\cdot NH_2$, is obtained when ethyleneacetonitrile (Abstr., 1899, i, 676) is reduced with sodium and absolute alcohol; it is a colourless liquid boiling at 88° and soluble in water; on treatment with nitrous acid, it yields a small amount of *trimethylenecarbinol* (*ethylene ethyl alcohol*),

$\left.\begin{matrix}CH_2\\|\\CH_2\end{matrix}\right>CH\cdot CH_2\cdot OH$, boiling at 130° under 756 mm. pressure. *Trimethylenecarboxylic chloride*,

$\left.\begin{matrix}CH_2\\|\\CH_2\end{matrix}\right>CH\cdot COCl$, boils at 120—122° under 754 mm. pressure. A comparison of the boiling points of these compounds with those of the corresponding *iso*butyl derivatives indicates that the loss of two hydrogen atoms accompanying the conversion of $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C$ into $\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>\!C$ produces an increase of 21—27° in the boiling point. J. J. S.

Carbamide as the Product of Oxidation of Nitrogenous Substances. By ADOLF JOLLES (*J. pr. Chem.*, 1901, [ii], 63, 516—522. Compare this vol., i, 30, 262).—The experiments on the oxidation of amides by means of permanganate (*loc. cit.*) are continued. Lactamide and succinamide, when oxidised, yield the whole of their nitrogen as carbamide. Although from aspartic acid (*loc. cit.*) and benzamide carbamide is not produced, yet the whole of the nitrogen of benzoylaspartic acid is quantitatively converted into carbamide in the oxidation.

In the experiments, the amide is oxidised by permanganate in the presence of very dilute sulphuric acid. The total nitrogen in the liquid is determined, and the carbamide precipitated as oxalate, and estimated. K. J. P. O.

Condensation of Acetone and Carbamide. By ARTHUR WEINSCHENK (*Ber.*, 1901, 34, 2185—2187).—*Triacetonedicarbamide*, $CMe_2(NH{\cdot}CO{\cdot}N{:}CMe_2)_2$, obtained by passing hydrogen chloride into acetone in which carbamide is suspended and boiling for 7 hours, crystallises (with $3H_2O$) in leaflets, melts at 265—268°, and, when heated at 140—150° with water, is decomposed into ammonia, acetone, and carbon dioxide. R. H. P.

The Thiocarbimide from the Seeds of Brassica Napus (Colza). By B. SJOLLEMA (*Rec. trav. Chim.*, 1901, 20, 237—242).—A crotonylthiocarbimide is obtained when colza seeds are freed from oil, treated with myrosin and water, and finally distilled in steam. It is an oil boiling at about 174° and having a sp. gr. 0·9933 at 11°/4°; it is optically inactive, and on treatment with alcohol and ammonia yields a crotonylthiocarbamide melting at 64°. This product does not appear to be identical with either of the compounds described by Hofmann (this Journ., 1874, 792) and Charon (Abstr., 1899, i, 849). J. J. S.

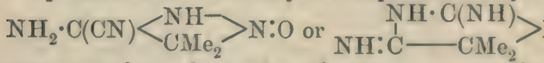
Existence of Derivatives of Quadrivalent Nitrogen. II. By OSCAR PILOTY and B. GRAF SCHWERIN (*Ber.*, 1901, 34, 2354—2367. Compare this vol., i, 517).—Both porphyrexin and porphyrexide are converted by the action of chlorine into a mono- and a di-chloroporphyrexide.

Chloroporphyrexide, $C_5H_8ON_4Cl$, prepared by the action of a concentrated solution of bleaching powder on an aqueous suspension of porphyrexide, crystallises in rhombic plates melting and decomposing at 152°, which are wine-red by transmitted light, and of a greenish-golden, metallic colour by reflected light. The mol. weight determined in acetic acid corresponded with the above formula. Concentrated nitric acid converts it into an ochre-yellow, crystalline mass, which is probably the nitrate; with water, the original chloroporphyrexide is immediately regenerated. It dissolves in sodium hydroxide and ammonia, forming a deep cherry-red solution. The *silver* salt, $C_5H_7ON_4ClAg$, prepared from the solution of the ammonium salt, forms a carmine-red, crystalline powder decomposing at 170°.

Dichloroporphyrexide, $C_5H_7ON_4Cl_2$, prepared by the action of chlorine on porphyrexide suspended in water, forms a red powder melting and decomposing at 117—118°, and readily soluble in ether or chloroform. The mol. weight, determined in benzene, corresponded with the above formula. In the moist state, it is rapidly converted into the monochloro-derivative, with evolution of chlorine. All the basic properties of porphyrexide have disappeared, and with concentrated nitric acid the nitrate (?) of monochloroporphyrexide is formed with evolution of chlorine. With concentrated ammonia, this compound explodes. Despite its instability, it dissolves in dilute ammonia or sodium hydroxide, forming salts. The *sodium* salt crystallises in deep violet-blue, rhombic plates melting and exploding at 145°; with dilute sulphuric acid, dichloroporphyrexide is reformed. The *ammonium* salt forms sparingly soluble needles of deep violet colour, closely resembling murexide crystals, and decomposing violently at 96°. The *silver* salt forms a nearly black powder exploding at 150°, and is neither decomposed by light nor by long keeping.

The two chloroporphyrexides, as well as porphyrexide, react with hydrogen peroxide, evolving oxygen both in acid and alkaline solution; with hydrochloric acid, chlorine is evolved; with hydrogen sulphide, sulphur is set free; with hydriodic acid, iodine is liberated and porphyrexine formed. Quantitative experiments show that 1 mol. of porphyrexide liberates from hydriodic acid 1 atom of iodine; 1 mol. of chloroporphyrexide 3 atoms of iodine; and 1 mol. of dichloroporphyrexide 5 atoms of iodine. Each atom of chlorine sets free 2 atoms of iodine. This fact, with others, shows that the chlorine atoms have replaced hydrogen which was attached to nitrogen atoms.

The authors discuss the constitution of porphyrexide, and from the fact that it has a molecular weight, expressed by the formula $C_5H_9ON_4$, and from its relation to porphyrexine and to the two chloroporphyrexides, and finally from its behaviour towards reducing agents (hydriodic acid), conclude that it contains the group $(:N:O)$, in which nitrogen is quadrivalent. It may be represented by one of the formulæ



$NH_2\cdot C(CN)<\begin{matrix}NH-\\CMe_2\end{matrix}>N:O$ or $\begin{matrix}NH\cdot C(NH)\\ | \\ NH:C\text{——}CMe_2\end{matrix}>N:O$. Porphyrexide is consequently a derivative of nitrogen peroxide, and exhibits many properties resembling those of this substance. K. J. P. O.

Ammonia Nickel Cyanide. By A. Bernoulli and E. Grether (*Chem. Zeit.*, 1901, **25**, 436—437).—A solution of nickel cyanide in concentrated ammonia, when kept, yields large, violet-blue, flat needles which quickly become transformed into paler and smaller needles having the composition $NiC_2N_2,2NH_3,H_2O$. When heated at 250°, this is converted into nickel cyanide; it is only slowly decomposed by water or dilute acids, and is soluble in ammonium hydroxide, carbonate, sulphide, or oxalate, and also in potassium cyanide solution.

J. J. S.

Influence of Light on the Decomposition of Aqueous Solutions of Potassium Ferricyanide. By J. Matuschek (*Chem. Zeit.*, 1901, **25**, 522—523. Compare this vol., i, 455).—Solutions of potassium ferricyanide containing 5 grams or less of the salt in 100 grams of water follow the generalisation previously given.

The decomposition is complete in all cases, that is, all the iron may be precipitated as ferric hydroxide under the influence of sunlight. The rate of decomposition is greater the brighter the sunlight.

J. J. S.

Derivatives of *m*-Dibromodinitrobenzene. By C. Loring Jackson and Wallace P. Cohoe (*Amer. Chem. J.*, 1901, **26**, 1—9).—When bromine is added to bromoacetanilide suspended in water, *s*-tribromoaniline is produced, whilst by the action of bromine on the same substance suspended in glacial acetic acid or chloroform, a good yield of dibromoacetanilide is obtained. If dibromoaniline, prepared by the hydrolysis of dibromoacetanilide, is treated with nitrous acid, dibromobenzene is produced, which, on nitration, yields 1 : 3-dibromo-4 : 6-dinitrobenzene melting at 117°. By the action of aniline at 100° on dibromodinitrobenzene, 4 : 6-dinitro-1 : 3-dianilinobenzene is formed, identical with that obtained by Nietzki and Schedler (Abstr., 1897, i, 464) from 1 : 3-dichloro-4 : 6-dinitrobenzene.

Bromodinitroanilinobenzene, $NHPh\cdot C_6H_2Br(NO_2)_2$, obtained by the action of aniline on well-cooled dibromodinitrobenzene, is soluble in benzene, toluene, or chloroform, and occurs in two modifications; the yellow modification crystallises in short, thick, flat prisms or rhombic plates and melts at 157°, whilst the red modification forms square prisms, and, when heated to 135°, is completely converted into the yellow form. If a solution of the yellow form in benzene is allowed to evaporate, a red oil is deposited, which, on stirring, solidifies to crystals of the red modification.

When *m*-dibromodinitrobenzene is treated with sodium ethoxide, dinitroresorcinol diethyl ether is produced. *Dinitroresorcinol diphenyl ether*, $C_6H_2(OPh)_2(NO_2)_2$, obtained by the action of sodium phenoxide on dibromodinitrobenzene, crystallises in slender, white prisms, melts at 129°, and is soluble in benzene, toluene, or chloroform; when this compound is dissolved in alcoholic ethyl sodiomalonate, phenol is eliminated, and *ethyl phenoxydinitrophenylmalonate*,

$$OPh\cdot C_6H_2(NO_2)_2\cdot CH(CO_2Et)_2,$$

is obtained as a pale yellow oil which yields a bright red *sodium* derivative.

When dibromodinitrobenzene is reduced with zinc dust and acetic acid, 1 : 3-dibromo-4 : 6-phenylenediamine is produced, identical with that obtained by Jackson and Calvert (Abstr., 1896, i, 538) by the action of bromine on *m*-phenylenediacetamide.

E. G.

Action of Sodium Sulphite on Tribromodinitrobenzene and Tribromotrinitrobenzene. By C. Loring Jackson and Richard B. Earle (*Amer. Chem. J.*, 1901, **26**, 46—55).—When an alcoholic solution of 1 : 3 : 5-tribromo-2 : 4-dinitrobenzene is boiled for 5 hours with sodium sulphite, 1 : 3-dibromo-4 : 6-dinitrobenzene is produced. If 1 : 3 : 5-tribromo-2 : 4 : 6-trinitrobenzene is treated in a similar manner, 1 : 3-*dibromo*-2 : 4 : 6-*trinitrobenzene* is obtained, which crystallises from benzene in pale yellow prisms with a slight greenish tinge, melts at 135°, and is soluble in ether, chloroform, acetone, or alcohol.

When dibromodinitrobenzene is heated with a mixture of fuming nitric and strong sulphuric acids, tribromodinitrobenzene is produced, together with a small quantity of dibromotrinitrobenzene. 1 : 2 : 3-*Tribromo*-4 : 6-*dinitrobenzene* crystallises in yellowish-white, rectangular plates, melts at 150°, and is soluble in benzene, ether, chloroform, glacial acetic acid, acetone, or alcohol.

By the action of sodium ethoxide on dibromotrinitrobenzene, styphnic diethyl ether is produced. Sodium ethoxide reacts with tribromodinitrobenzene with formation of *bromodinitroresorcinol ethyl ether*, $OH\cdot C_6HBr(NO_2)_2\cdot OEt$, which crystallises from alcohol in white, feathery needles, and melts at 78°; its *barium* salt is described. The bromodinitroresorcinol ethyl ether is accompanied by a small quantity of another *substance*, which crystallises in long, white needles, melts at 58°, and is probably the corresponding diethyl ether. E. G.

Symmetrical Tri-iodobenzene. By C. Loring Jackson and G. E. Behr (*Amer. Chem. J.*, 1901, 26, 55—61).—1:3:5-Tri-iodobenzene, prepared from tri-iodoaniline by means of the diazo-reaction, crystallises from alcohol in long, white prisms, melts at 181°, sublimes readily, and is soluble in benzene, carbon disulphide, chloroform, ether, glacial acetic acid, ethyl acetate, alcohol, or acetone; it is identical with the compound obtained by Istrati and Georgescu (Abstr., 1892, 1310) by heating together benzene, iodine, and concentrated sulphuric acid, and regarded by them as 1 : 2 : 3-tri-iodobenzene. When tri-iodobenzene is treated with fuming nitric acid, it yields tri-iododinitrobenzene, which melts at 210°, and is converted by aniline into trianilinodinitrobenzene, identical with that obtained by Palmer and Jackson (Abstr., 1890, 248) from 1 : 3 : 5-tribromo-2 : 4-dinitrobenzene. E. G.

Syntheses in the Diphenyl Series. By Fritz Ullmann and Jean Bielecki (*Ber.*, 1901, 34, 2174—2185).—Very good yields of symmetrically substituted diphenyl compounds can be obtained by heating haloid derivatives of the benzene hydrocarbons, either alone or dissolved in nitrobenzene, with copper powder; for example, *o*-bromonitrobenzene, when heated with copper powder, yields 2 : 2′-dinitrodiphenyl. The following new compounds are described: 3 : 3′ : 4 : 4′-*tetranitrodiphenyl* (prepared from 4-*iodo*-1 : 2-*dinitrobenzene*, obtained by the nitration of *m*-iodonitrobenzene, and forming yellow crystals melting at 74·5°), which crystallises in yellow prisms and melts at 186°; 2 : 2′ : 4 : 4′ : 6 : 6′-*hexanitrodiphenyl* (from picryl chloride), which forms large, brownish crystals (with $\frac{1}{2}C_6H_5Me$) melting at 238°; 4:4′-*dichloro*-2 : 2′-*dinitrodiphenyl* (from 1 : 4-dichloro-2-nitrobenzene), which forms yellow crystals melting at 136°, and the analogous *bromo*-derivative, which crystallises in yellow needles melting at 138°; *methyl* 2 : 2′-*dinitrodiphenyl*-4 : 4′-*dicarboxylate* (from *methyl* 4-*bromo*-3-*nitrobenzoate*, crystallising in large, lustrous needles and melting at 104°), which crystallises in large prisms and melts at 159—160°; *methyl* 2 : 2′ : 6 : 6′-*tetranitrodiphenyl*-4 : 4′-*dicarboxylate* (from *methyl* 4-*chloro*-3 : 5-*dinitrobenzoate*, melting at 175°), which crystallises in colourless needles and melts at 173°. A 74 per cent. yield of 1 : 1′-dinaphthyl is obtained by heating α-iodonaphthalene with copper powder. R. H. P.

Electrolytic Reduction of Aromatic Nitro-compounds to Amines. By A. CHILESOTTI (*Zeit. Elektrochem.*, 1901, 7, 768—773).—The nitro-compound is made into an emulsion with hydrochloric or sulphuric acid of sufficient strength to leave the solution 0·7 to 0·8*N* after reduction is complete. This emulsion is placed in a jar with a cathode of nickel gauze. A porous pot contains the lead anode immersed in 9 per cent. sulphuric acid. A current density of about 0·12 ampere per sq. cm. is employed. The temperature rises to 40—50°. To the cathode solution, a little tin, copper, or iron salt is added. The tin salts give the best results. The yields, as regards both current and material, are almost quantitative. The spongy metal which is deposited on the cathode during the reduction is the active agent. A cathode of copper gauze without added salt gives a very incomplete reduction. The fact that copper gives almost as good results as tin shows that the metals do not act primarily on the nitro-compounds, which are hardly reduced by copper. It is also improbable that the nitroso-compound which is the first reduction product is acted on, because it is found that by the action of finely divided copper, nitrosobenzene yields large quantities of azoxy- and azo-benzene in addition to aniline. Phenylhydroxylamine is, however, very rapidly reduced to aniline by finely divided copper. The author therefore supposes that the nitro-compounds are first reduced to the corresponding hydroxylamine derivatives, as is always the case, and that these are then very rapidly reduced to amines by the spongy metals. The metals of course go into solution, but are immediately reprecipitated by the current. T. E.

Oxidation of Benzylamine. By EUGEN BAMBERGER and THOR SCHEUTZ (*Ber.*, 1901, 34, 2262—2272. Compare Abstr., 1899, i, 347, 682; this vol., i, 200).—The oxidation of fatty bases, such as benzylamine, ethylamine, &c., by Caro's reagent, proceeds much more slowly than that of aromatic bases, and is also much slower than that of the first products of the oxidation, so that it is difficult to obtain the latter in any quantity. In the case of benzylamine, the chief product is benzoic acid, in addition to which the following have been isolated: benzaldoxime, benzonitrile, benzhydroxamic acid, phenylnitroethane, and benzaldehyde. Indications of the presence of benzamide and phenylnitrolic acid were also obtained, and three neutral substances melting at 205°, 100—103°, and about 100°, and a colourless base, which forms yellow solutions in acids, were isolated.

It appears probable that the first stage of the oxidation consists in the formation of benzylhydroxylamine, which, however, at once passes by oxidation into benzaldoxime. This seems to constitute the typical distinction between the behaviour of aromatic and fatty bases towards Caro's reagent. The aromatic bases yield the corresponding hydroxylamine, which is then further oxidised to a nitroso-compound and finally to a nitro-compound.

The benzaldoxime is then partly converted into benzonitrile, partly into benzohydroxamic acid, and partly into *iso*phenylnitromethane, $CHPh:NO_2H$, which at once passes into phenylnitromethane, $CH_2Ph\cdot NO_2$.

The production of benzonitrile in this reaction supplies the converse of Mendius' well known reduction of the nitriles to amines. A. H.

Nitro- and Bromo-derivatives of the Xylidines. By Emilio Noelting, A. Braun, and G. Thesmar (*Ber.*, 1901, **34**, 2242—2262).—Both *o*-3- and *o*-4-xylidine yield, on nitration, all three possible mononitro-derivatives, whilst Noelting and Stoecklin (Abstr., 1891, 692) previously only obtained two of these from each base. The statements previously made are therefore to be replaced by those now published. The nitro-derivatives of *o*-3-xylidine may be obtained either by nitrating the corresponding acetylxylidide or by the direct nitration of the base at a low temperature in presence of sulphuric acid. In the former case, the separation of the three products may be carried out by distillation with steam and is very tedious, the relative proportions formed being 30 per cent. of 4-, 13 per cent. of 5-, and 55 per cent. of 6-nitro-*o*-3-xylidine. The yield obtained by direct nitration varies, the amount of 5-nitro-compound increasing with the amount of sulphuric acid employed. Using 20 parts of sulphuric acid, there was formed 25 per cent. of 3-, 45 per cent. of 5-, and 30 per cent. of 6-nitro-compound. 4-*Nitro*-o-3-*xylidine* crystallises in brick-red, lozenge-shaped tablets melting at 118—119°, and only dissolves in concentrated hydrochloric acid. The *acetyl* derivative crystallises in colourless needles melting at 160°, and the *benzoyl* derivative melts at 177—178°. 5-*Nitro*-o-3-*xylidine* crystallises in light yellow needles melting at 111—112°, and has more strongly basic properties than the foregoing compound. The *acetyl* derivative crystallises in needles melting at 230—231°, whilst the *benzoyl* derivative melts at 227—228°. 6-*Nitro*-o-3-*xylidine* forms brownish-yellow prisms melting at 114°. The *acetyl* derivative crystallises in faintly yellow needles melting at 149—150°, and the *benzoyl* derivative melts at 208—209°.

o-4-Xylidine also yields three mononitro-derivatives, the relative proportions, when the nitration is carried out in presence of sulphuric acid, being 47 per cent. of 5-, 31 per cent. of 3-, and 13 per cent. of 6-*nitro*-o-4-*xylidine*. 5-*Nitro*-o-4-*xylidine* crystallises in brownish-red prisms melting at 139—140°, and forms salts which are decomposed by water. The *acetyl* derivative crystallises in small, light yellow needles melting at 107°, and the *benzoyl* derivative in light yellow, silky needles melting at 149—150°. 3-*Nitro*-o-4-*xylidine* crystallises in scarlet-red prisms melting at 65—66°, and is readily volatile with steam. The *acetyl* derivative forms small needles melting at 115—116°, and the *benzoyl* compound sparingly soluble needles melting at 199—200°. 6-*Nitro*-o-4-*xylidine* crystallises in long, lustrous, orange-coloured plates melting at 74—75°. The *acetyl* derivative crystallises in small needles melting at 209—210°, whilst the *benzoyl* derivative melts at 223—224°.

The four isomeric xylylenediamines can all be prepared by the reduction of the mononitro-*o*-xylidines. o-3 : 4-*Xylylenediamine* crystallises in colourless plates melting at 89°, and, like the other isomerides, is quite stable in the air when dry. o-4 : 5-*Xylylenediamine* also forms plates, and melts at 125—126°, whilst o-3 : 5-*xylylenediamine* crystallises in small needles melting at 66—67°, and o-3 : 6-*xylylenediamine* separates in faint brown-coloured prisms melting at 116°, and can also be prepared by treating *o*-3-xylidine with diazobenzene-*m*-sulphonic acid and decomposing the azo-compound produced with tin and hydrochloric acid.

Monobromo-derivatives of m-4-*xylidine*.—6-Bromo-*m*-4-xylidine has previously been prepared by Genz (*Ber.*, 1870, 3, 225), and can also be obtained from 4-nitro-*m*-6-xylidine by replacing the amino-group by bromine and then reducing. It melts at 99—100°, whilst the *acetyl* derivative melts at 168—179°. The p-*nitrobenzylidene* derivative, $C_6H_2BzMe_2\cdot N\colon CH\cdot C_6H_4\cdot NO_2$, forms yellow needles melting at 139°. The corresponding 6-*bromo*-m-4-*xylenol* crystallises in colourless needles melting at 72°. 2-*Bromo*-m-4-*xylidine* is prepared from 4-nitro-*m*-2-xylidine in a similar manner to the foregoing compound. 2-*Bromo*-4-*nitro*-m *xylene* crystallises in soft, light yellow needles which melt at 57—58°. 2-*Bromo*-m-4-*xylidine* crystallises in long, colourless, silky needles melting at 47—48°. The *acetyl* derivative melts at 151—152°, and the p-*nitrobenzylidene* derivative at 182—183°. The corresponding 2-*bromo*-m-4-*xylenol* crystallises in light yellow needles melting at 68°. 5-Bromo-*m* 4-xylidine, also melting at 47—48°, is formed by the direct bromination of *m*-4-xylidine, and has previously been described by Fischer and Windaus (Abstr., 1900, i, 484), who proved its constitution by converting it into mesitylenic acid. The *acetyl* derivative melts at 196—197°, the p-*nitrobenzylidene* derivative at 130°, and the corresponding 5-*bromo*-m-4-*xylenol* at 72°. 5-Bromo-*m*-4-xylidine can be prepared indirectly by two methods, each of which shows its constitution. 4-Nitro-*m*-6-xylidine yields, on bromination, 5-*bromo*-4-*nitro*-m-6-*xylidine*, which crystallises in large prisms melting at 66—67°. 5-*Bromo*-4-*nitro*-m-*xylene*, prepared from the foregoing by elimination of the amino-group, crystallises in flat, faintly yellow needles melting at 39—40°, and is converted by reduction into the desired 5-*bromo*-m-4-*xylidine*. According to the second method, 4-nitro-*m*-5-xylidine is converted by the diazo-reaction into the corresponding 5-bromo-derivative, and this, on reduction, yields the 5-bromo-*m*-4-xylidine.

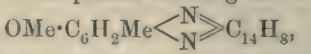
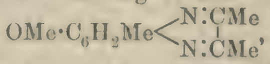
Bromo-derivatives of m-2-*xylidine*.—4-*Bromo*-m-2-*xylidine* is best prepared synthetically from 2-nitro-*m*-xylene, which is converted by nitration into 2 : 4-dinitro-*m*-xylene, and on reduction with alcoholic ammonium sulphide, this compound yields 2-*nitro*-4-*amino*-m-*xylene*, which crystallises in long, golden, lustrous needles melting at 81—82°, and is readily converted by the diazo-reaction into 4-*bromo*-2-*nitro*-m-*xylene*, crystallising in yellowish prisms melting at 70—71°. Finally, this compound yields on reduction 4-bromo-*m*-2-xylidine, which forms lustrous, colourless needles melting at 21·5° to a colourless oil which boils at 146—147° under 15 mm. pressure. The *acetyl* derivative, crystallising in small needles melting at 136°, is best prepared indirectly from 4-nitro-*m*-2-acetylxylidide, which is converted by reduction and replacement of the resulting amino-group by bromine into this compound; it was, however, found impossible to prepare the free base from it by hydrolysis.

5-Bromo-*m*-2-xylidine, which is the only remaining isomeride, has been previously prepared by Fischer and Windaus (*loc. cit.*), who, however, did not ascertain its constitution. The bromination of *m*-2-acetylxylidide leads to the formation of a mixture of 4- and 5-bromoderivatives. A. H.

Camphoric Acid Phenetidide. By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1901, 25, 445).—*Camphoric acid phenetidide*,

$$C_8H_{14}{<}\begin{matrix}CO\\CO\end{matrix}{>}N\cdot C_6H_4\cdot OEt,$$

is obtained when the product formed by the action of camphoric acid on *p*-phenetidine is crystallised several times from water and alcohol. It crystallises in plates, melts at 112°, and may probably be of use in cases of tuberculosis. J. J. S.

Orientating influence of the Methoxy-group on the Nitro-group. By FELIX KAUFLER and FRANZ WENZEL (*Ber.*, 1901, 34, 2238—2242).—Whilst the presence of a nitro-group in the benzene nucleus favours the entrance of a second nitro-group in the meta-position, that of a hydroxyl group favours the production of ortho- and para-compounds. When both groups are present simultaneously, the influence of the hydroxyl group preponderates, and ortho- and para-dinitro-compounds are obtained by nitration. The following experiments prove that the methoxy-group has the same directing influence as the hydroxyl group. *o*-Nitro-*p*-cresol methyl ether is readily converted by nitration in acetic acid solution into *dinitro*-p-*cresol methyl ether*, $C_6H_2Me(NO_2)_2\cdot OMe$, which crystallises in colourless needles melting at 126—128°. On reduction, it yields *diamino*-p *cresol methyl ether*, which crystallises in long, lustrous prisms melting at 72—73°. 13-*Methoxy* 10-*methylphenanthrazine*,  $OMe\cdot C_6H_2Me{<}\begin{matrix}N\\N\end{matrix}{\gg}C_{14}H_8$, is obtained when the base is treated with phenanthraquinone, and crystallises in light yellow, lustrous needles melting at 265—268°. 8-*Methoxy-2 : 3 : 5-trimethylquinoxaline*,  $OMe\cdot C_6H_2Me{<}\begin{matrix}N{:}CMe\\ |\\ N{:}CMe\end{matrix}$, is obtained by the action of diacetyl on the base, and crystallises in thin, colourless needles melting at 125°. The constitution of the dinitro-compound must therefore be

$$C_6H_2Me(OMe)(NO_2)_2\quad [Me{:}NO_2\cdot NO_2\cdot OMe = 1:2:3:4],$$

so that the second nitro-group has entered in the ortho-position to the one already present. *p*-Nitro-*o*-cresol methyl ether is not acted on by concentrated nitric acid alone, but in the presence of sulphuric acid yields *trinitro*-o-*cresol methyl ether*, which crystallises in long, colourless needles melting at 111—112°. This compound is the methyl ether of Noelting's trinitro-*o*-cresol (Abstr., 1884, 1007), and must contain at least two nitro-groups in the ortho-position to one another. A. H.

Benzylcarvacrol and Benzyl-*m* cresol. By G. ANTONIO VENTURI (*Gazzetta*, 1901, 31, i, 469—474).—*Benzylcarvacrol*,

$$CH_2Ph\cdot C_6H_2MePr^{\beta}\cdot OH,$$

obtained by the action of benzyl alcohol on carvacrol in presence of zinc chloride, boils at 235—240° under 50 mm. pressure. Its *acetyl* derivative, $C_{19}H_{22}O_2$, is a dense, oily, pale yellow liquid boiling at 230° under 30 mm. pressure.

Benzyl-m-*cresol*, $CH_2Ph\cdot C_6H_3Me\cdot OH$, separates from benzene in acicular crystals melting at 93—93·5°. Its *acetyl* derivative, $C_{16}H_{16}O_2$, is deposited from light petroleum in tabular crystals melting at 46·5°.

T. H. P.

Nitration of Ortho- and Meta-chloro- and -bromo-benzoic Acids. By ARNOLD F. HOLLEMANN and B. R. DE BRUYN (*Rec. trav. Chim.*, 1901, **20**, 206—234. Compare Rhalis, *Annalen*, 1879, **198**, 109).—*o*-Chlorobenzoic acid, when added to nitric acid of sp. gr. 1·52 at the ordinary temperature, yields a mixture of 2-chloro-5-nitro- with a little 2-chloro-3-nitro-benzoic acid. The two acids are best separated by fractional crystallisation of their potassium salts from concentrated aqueous solutions. 2-*Chloro-3-nitrobenzoic acid* melts at 185°, is only sparingly soluble in water, and when heated with alcoholic ammonia in sealed tubes, yields Hübner's 3-nitro-2-aminobenzoic acid (*Annalen*, 1879, **195**, 37).

o-Bromobenzoic acid, when treated in the same manner, yields 2-bromo-5-nitrobenzoic acid melting at 180° (compare Rhalis, *loc. cit.*), and 2-*bromo-3-nitrobenzoic acid* melting at 191°.

m-Chlorobenzoic acid yields a mixture of 3-chloro-6-nitrobenzoic acid melting at 139° and 3-chloro-2-nitrobenzoic acid melting at 235°; the two acids are best separated by fractional crystallisation from ether, when crystals of the chief product, the 3 : 6-acid, are obtained, the ethereal mother liquor is evaporated, and the dry residue extracted several times with small amounts of warm benzene and finally crystallised from alcohol.

When dilute hydrochloric acid is added to a cold solution of potassium 3-chloro-6-nitrobenzoate, an *acid potassium* salt, $C_{14}H_7O_8N_2Cl_2K$, separates.

m-Bromobenzoic acid yields as its chief product of nitration 3-bromo-6-nitrobenzoic acid melting at 140°, together with 3-bromo-2-nitrobenzoic acid melting at 250°. The two acids are separated by fractional crystallisation from cold dilute alcohol (65 per cent. by vol.) and subsequent crystallisation of the sodium salts from water. The 3-bromo-6-nitro-acid forms definite compounds with benzene and its homologues.

The determinations of the amount of each isomeride formed in the different cases has been made by taking the solidifying point and comparing it with the solidifying point of mixtures of known composition. The paper concludes with a criticism on the rules for substitution in the benzene nucleus.

J. J. S.

Structure of Kalle and Co.'s *o*-Chlorodinitrobenzoic Acid. By ARNOLD F. HOLLEMAN (*Rec. trav. Chim.*, 1901, 20, 235—236).—Kalle and Co.'s *o* chlorodinitrobenzoic acid (*Chem. Centr.*, 1900, i, 742) may be obtained by the nitration of 2-chloro-3-nitrobenzoic acid and also of the 2-chloro-5-nitro-acid, and must hence be 2-chloro-3 : 5-dinitrobenzoic acid.

J. J. S.

Action of Formaldehyde on Methyl *o*-Aminobenzoate. By HUGO ERDMANN (*J. pr. Chem.*, 1901, [ii], **63**, 569—572. Compare this vol., i, 536).—Mehner (this vol., i, 470) obtained from methyl *o*-aminobenzoate and formaldehyde methyl methylenedi-*o*-aminodibenzoate, whilst the author (*loc. cit.*) observed the formation of methyl methylene-*o*-aminobenzoate. The author finds that the reaction takes place in three stages; first, methyl methylene-*o*-aminobenzoate is formed; 2 mols. of this substance then interact with elimination of formaldehyde, and the formation of a *compound*, $C_{17}H_{18}O_4N_2,H_2O$, which is obtained by crystallising from dilute alcohol, the crude product of the action of formaldehyde on methyl *o*-aminobenzoate, and separates in needles melting at 117°. This compound is then transformed into the methylenediamino-compound described by Mehner. The conditions by which this transformation is effected could not be exactly determined. K. J. P. O.

Action of Pure Nitric Acid on the three Toluic Acids and on their Derivatives. By L. van Scherpenzeel (*Rec. trav. Chim.*, 1901, **20**, 149—182).—When *p*-toluic acid is nitrated at 0°, it yields 2-nitro-*p*-toluic acid, [$Me:NO_2:CO_2H=1:2:4$], and at the ordinary temperature, 2 : 6-dinitro-*p*-toluic acid. The methyl ester, amide, and methylamide, when nitrated at 0°, yield derivatives of the 2-nitro-acid. The methylamide of *p*-toluic acid melts at 145—145·5° (compare Gattermann and Schmidt, Abstr., 1887, 358). The dimethylamide forms large, transparent crystals melting at 41° and distilling at 156° under 10 mm. pressure, and is readily soluble in most organic solvents. The *methylamide* of 2-nitro-*p*-toluic acid melts at 149°, and is readily soluble in hot water. When methyl *p*-toluate is nitrated at 20°, the product is methyl 2-nitro-*p*-toluate; *p*-toluamide at 20° yields the mononitro-acid, but the methylamide yields the 2 : 6-dinitro-acid, and the dimethylamide yields the dimethylamide of the dinitro-acid.

m-Toluic acid was prepared and purified by Ador and Rilliet's method (*Ber.*, 1879, **12**, 2300), a bye-product in the preparation of the acid is 6-nitro-*m*-toluic acid. *m*-Toluyl chloride melts at −23°, the methyl ester boils at 220·5—221°, Klages gives 214—215° (Abstr., 1899, i, 599), the amide forms scintillating crystals melting at 93—94°, the *methylamide* melts at 44·5—45°, and the *dimethylamide* is an oil distilling at 148° and having sp. gr. 1·043 at 15°. When nitrated at 0°, *m*-toluic acid yields a mixture of 4-nitro-*m*-toluic acid melting at 223° and 2-nitro-*m*-toluic acid melting at 184—185° (Jacobsen, Abstr., 1882, 185); the methyl ester, amide, and methylamide yield the derivatives of the two mono-nitro-acids, but the dimethylamide yields the dimethylamide of the 4-nitro-acid only. When nitrated at the ordinary temperature, the meta-acid yields 2 : 4-dinitro-*m*-toluic acid melting at 173°; this acid is also formed when the amide and methylamide of *m*-toluic acid or of 4-nitro-*m*-toluic acid are nitrated at the ordinary temperature. Methyl *m*-toluate, on nitration at the ordinary temperature, yields methyl 2 : 4-dinitro-*m*-toluate melting at 104—105°, but the dimethylamide of *m*-toluic acid yields the dimethylamide of 4-nitro-*m*-toluic acid.

*Methyl 4-nitro-*m*-toluate* melts at 71·5°, the *amide* crystallises in glistening needles melting at 191°, the *methylamide* in colourless plates melting at 135—136° and only sparingly soluble in ether, and the *dimethylamide* in colourless crystals melting at 88·5° and readily turning red on exposure to sunlight. The *amide* of 2-nitro-*m*-toluic acid melts at 135—136°.

Methyl *o*-toluate distils at 213° [Kellas (Abstr., 1898, i, 86) gives 207—208°] and has the sp. gr. 1·073 at 15°. The *methylamide* crystallises in colourless needles melting at 75°, the *dimethylamide* is a colourless liquid distilling at 147° and having the sp. gr. 1·033 at 25°. When nitrated at 0°, *o*-toluic acid yields a mixture of 4-nitro-*o*-toluic acid melting at 178—178·5° (compare Jacobsen and Wierss, Abstr., 1883, 1121) and 6-nitro-*o*-toluic acid melting at 184—184·5°; the latter is probably identical with Jacobsen and Wierss' β-nitro-acid melting at 145°. The two acids are best separated by fractional crystallisation of their methyl esters from methyl alcohol. The methyl ester, amide, methylamide, and dimethylamide of *o*-toluic-acid also yield the corresponding derivatives of the 4- and 6-nitro-acids when nitrated at 0°. When nitrated at the ordinary temperature, *o*-toluic-acid, as well as its two mononitro-derivatives, yields 4 : 6-dinitro-*o*-toluic acid (compare Jacobsen and Wierss, *loc. cit.*). The methyl ester under similar conditions yields methyl 4 : 6-dinitro-*o*-toluate melting at 73—73·5°. The amide and methylamide yield the 4 : 6-dinitro-acid, but the dimethylamide gives the 4-nitro-acid.

4-*Nitro-o-toluoyl chloride* crystallises in colourless needles melting at 59—60° and not readily decomposed by water, the *methyl ester* crystallises in oblong prisms and melts at 69°, the *methylamide* forms slender needles melting at 160°, and the *dimethylamide* melts at 105—106°. 6-*Nitro-o-toluoyl chloride* melts at 68—68·5°; the *methyl ester* forms pale yellowish needles melting at 66°, the *amide* colourless needles melting at 163°, the *methylamide* melts at 131—132°, and the *dimethylamide* at 69·5—70°. J. J. S.

New Bismuth Salicylate. By Paul Thibault (*J. Pharm.*, 1901, [vi], **14**, 22—25).—Bismuthic oxide, when treated on the water-bath with a strong solution of salicylic acid, yields *bismuth salicylate*, $Bi_2O_3(C_7H_6O_3)_3$, which crystallises in small, transparent prisms; when treated with warm water, boiling alcohol or ether, it yields salicylic acid, and, when fused, phenol. R. H. P.

Reduction of Indigotin in an Anhydrous Medium. By Arthur Binz (*J. pr. Chem.*, 1901, [ii], **63**, 497—516).—On heating indigotin in boiling naphthalene with zinc dust in the absence of oxygen, the blue solution rapidly becomes emerald-green. With completely anhydrous zinc dust or zinc amalgam, the same change occurs. On extracting the product in a specially adapted Soxhlet apparatus with boiling naphthalene in the absence of oxygen, the extract is at first green and later colourless. The latter extract becomes deep blue when air is admitted, and contains a substance yielding indigotin and zinc oxide. In order to determine the nature of this colourless substance, the action of boiling naphthalene on indigo-white or zinc indigo-white has been studied. Indigo-white dissolves in molten naphthalene with a red colour, and is converted into a substance which cannot again be oxidised to indigotin. *Zinc indigo-white*, $C_{16}H_{10}O_2N_2Zn$(?), prepared from calcium indigo-white and zinc chloride, and crystallising in lustrous leaflets, was extracted with boiling naphthalene; after the indigotin accompanying the zinc indigo-white had been removed, phenomena were observed identical with those previously described in the extraction of the product of the action of zinc dust on indigotin in boiling naphthalene. Zinc indigo-white is produced when indigo-white and zinc oxide are heated in boiling naphthalene; the solution thus obtained is emerald-green. The author concludes that zinc indigo-white is the chief product of the action of zinc dust on indigotin in boiling naphthalene. K. J. P. O.

Dibenzyldinitrile [4:4′-Dicyano-*s*-diphenylethane]. By P. Kattwinkel and Richard Wolffenstein (*Ber.*, 1901, 34, 2423—2425).—When *p*-toluonitrile is heated with aqueous potassium persulphate for 5—6 hours at 100°, 40 per cent. of it remains unchanged, and *p*-cyanobenzoic acid (7 per cent.) and 4:4′-*dicyano*-s-*diphenylethane*, $CN\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot C_6H_4\cdot CN$ (6 per cent.), are formed; the latter melts at 198°, and on hydrolysis with concentrated sulphuric acid yields the corresponding s-*diphenylethane*-4:4′-*dicarboxylic acid*, which does not melt at 320°.

p-Cyanobenzoic acid, which Sandmeyer has described (Abstr., 1885, 981) as melting at 214°, really melts at 219°; it can be crystallised from boiling water, and is not converted by this treatment into terephthalamic acid as stated by him. Sandmeyer's "terephthalamic acid" was only impure *p*-cyanobenzoic acid. W. A. D.

Attempted Synthesis of a γδ-Unsaturated Acid. By Fritz Fichter and Sylvain Hirsch (*Ber.*, 1901, 34, 2188—2191).—An attempt to obtain a γ-unsaturated acid by the partial reduction of an acid containing two double linkings in the β- and δ-positions. Cinnamaldehyde condenses with ethyl succinate in the presence of sodium ethoxide to form the hydrocarbon *αθ-diphenyl-αγεη-octatetrene*, $CHPh{:}CH\cdot[CH{:}CH]_2\cdot CH{:}CHPh$, which crystallises in transparent tablets melting at 124°, and *styrylitaconic acid*,

$$CHPh{:}CH\cdot CH{:}C(CO_2H)\cdot CH_2\cdot CO_2H,$$

which crystallises in lustrous, felted needles, melts and decomposes at 215—218°, and forms a microcrystalline *calcium* salt.

Phenethylidenepyrotartaric acid,

$$CH_2Ph\cdot CH{:}CH\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H,$$

obtained by reducing styrylitaconic acid in the cold with sodium amalgam, crystallises in tablets or needles, melts at 112°, forms crystalline *calcium* and *barium* salts, and when neutralised and boiled for 30 hours is transformed into *phenethylitaconic acid*,

$$CH_2Ph\cdot CH_2\cdot CH{:}C(CO_2H)\cdot CH_2\cdot CO_2H,$$

which crystallises in clusters of lustrous needles melting at 153° and forms an amorphous *calcium* salt. The latter acid, when reduced in warm acid solution with sodium amalgam, yields *phenethylpyrotartaric acid*, $CH_2Ph\cdot[CH_2]_2\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$, which crystallises in clusters of needles and melts at 83°. R. H. P.

Action of Sulphuryl Chloride on Ethyl Gallate. By Girolamo Mazzara and P. Guarnieri (*Gazzetta*, 1901, 31, i, 464—468).—*Ethyl dichlorogallate*, $C_6Cl_2(OH)_3\cdot CO_2Et$, prepared by the action of sulphuryl chloride (2 mols.) on ethyl gallate (1 mol.), separates from water, with $1\frac{1}{2}H_2O$, in faintly nacreous, colourless laminæ, melting at 121—128°, and showing a red tint when viewed in mass. After the removal of the water, the compound melts at 133—134°, at which temperature the long prismatic needles separating from benzene also melt. It dissolves slightly in chloroform, and is soluble also in dilute alkali carbonate solutions, giving a yellowish liquid which assumes successively a violet and a dark red coloration. In aqueous solutions, it gives a turquoise coloration with ferric chloride. Attempts to obtain dichlorogallic acid from the ethyl ester gave negative results. T. H. P.

Dihydroxyfluorescein. By CARL LIEBERMANN (*Ber.*, 1901, **34**, 2299—2303).—Hydroxyquinol condenses with phthalic anhydride to form a *dihydroxyfluorescein*, $C_{20}H_{12}O_7$, which crystallises in lustrous, greenish-golden, microscopic leaflets and forms a crystalline *tetracetate* melting at 264°; it dyes unmordanted wool and silk orange and gives good colours with mordanted cotton. R. H. P.

Lichens and their Characteristic Constituents. VI. By OSWALD HESSE (*J. pr. Chem.*, 1901, [ii], **63**, 522—553. Compare Abstr., 1898, i, 531, 679; 1899, i, 381; this vol., i, 85, 149, 546).—*Usnea longissima* contains only *d*-usnic acid ($[\alpha]_D$ +490·3° at 15° in chloroform solution), and not *l*-usnic acid as found by Salkowski (this vol., i, 152). This acid is a phenolcarboxylic acid, which yields normal salts, $C_{18}H_{15}O_7M'$, and basic salts. The *barium* salt, $(C_{18}H_{15}O_7)_2Ba,4H_2O$, prepared from very dilute solutions of usnic acid and barium hydroxide, forms yellowish-white crystals, the basic *strontium* salt, $C_{18}H_{14}O_7Sr,2H_2O$, yellow prisms.

Usnidic acid, $C_{18}H_{18}O_8,2H_2O$, prepared by fusing *d*-usnic acid for a very short time with potash, crystallises in white needles, which melt and decompose at 195°, and is a monobasic acid, giving in alcoholic solution a bluish-green coloration with ferric chloride, and readily oxidising in alkaline solution.

Alectoria jubata = *Bryopogon jubatum* var. *implexum* = *Alectoria implexa* = *Alectoria jubata* var. *cana* (gathered in the Tyrol), contains in the outermost cell-layers bryopogonic acid and in the inner alectoric acid; the mixture of these is Zopf's salazinic acid (Abstr., 1898, i, 90). These two acids can be separated by acetic acid, in which alectoric acid is insoluble.

Bryopogonic acid, $C_{28}H_{22}O_{14}$, crystallises in small, colourless needles, decomposing at 260°, and in alcoholic solution gives a brownish-red coloration with ferric chloride. It is readily soluble in alkalis and alkali carbonates, the solutions quickly becoming dark red. iso*Bryopogonic acid*, $C_{28}H_{22}O_{14}$, is formed when a solution of bryopogonic acid in potassium hydroxide is left to stand; hydrochloric acid precipitates the acid as a red, amorphous powder, which can be crystallised from acetic acid. It melts at a very high temperature and gives a dark brown coloration with ferric chloride in alcoholic solution.

Evernia furfuracea was found to contain no erythric or olivetoric acid (compare Zopf, this vol., i, 87), but together with atranorin a new monobasic acid, *evernuric acid*, $C_{22}H_{24}O_8$, crystallising in small, colourless needles melting at 191—192°; its alcoholic solution gives a violet coloration with ferric chloride and a yellow with bleaching powder; when boiled with barium hydroxide, carbon dioxide is eliminated; and its ammoniacal solution gives a precipitate with barium chloride.

Parmelia acetabulum contains salazinic acid. On keeping a solution in potassium hydroxide, the *potassium* salt, $C_{28}H_{20}O_{12}K_4$, of rubidic acid is obtained as scarlet, prismatic crystals; *rubidic acid*, $C_{28}H_{24}O_{12}$, forms a brick-red powder which decomposes at a high temperature. A solution of the potassium salt oxidises in the air, yielding an *acid*, $C_{28}H_{20}O_{11}$, which forms hard, black lumps.

Parmelia glabra, from the Black Forest, contains lecanoric acid, (m. p. 166°).

Pannaria lanuginosa yields two acids, *hydroxyroccelic acid*, $C_{17}H_{32}O_5$, which crystallises in colourless, flattened needles melting at 128°, and is precipitated by barium hydroxide; and *pannaric acid*, $C_9H_8O_4,1\frac{1}{2}$ or $2H_2O$, a monobasic acid, which crystallises in small, six-sided prisms melting at 224°, and is not precipitated by barium hydroxide; in alcoholic solution, it gives a blue coloration with ferric chloride, and with concentrated sulphuric acid yields a quinhydrone (?) as steel-blue needles.

Gyrophora polyphylla contains two acids, gyrophoric acid, which, with acetic acid yields orsellic acid, and, with alcohol, orcinol and ethyl orsellate; and umbilicaric acid, $C_{24}H_{19}O_9{\cdot}OMe$, which crystallises in colourless leaflets melting at 185—186°, and with hydriodic acid yields methyl iodide and orcinol; the *potassium* salt, $C_{25}H_{20}O_{10}K_2,5H_2O$, forms a colourless, crystalline powder. Boiling barium hydroxide converts it into orcinolcarboxylic and *umbilicarinic acid*, $C_{16}H_{13}O_6{\cdot}OMe$, which crystallises in colourless needles melting and decomposing at 180°, and with ferric chloride gives a violet coloration.

Blastenia arenaria contains blastenin and phytosterol. *B. percrocata* contains blastenin, but no chrysophanic acid.

Urceolaria scruposa yields lecanoric and traces of a second acid.

Pertusaria corallina = *Pertusaria ocellata β corallina* = *Isidium corallinum* contains *ocellatic acid*, $C_{20}H_{15}O_{11}{\cdot}OMe$, which forms microscopic, crystalline aggregates melting and decomposing at 208°, and with ferric chloride gives a purple-violet coloration; the *potassium* salt forms colourless needles.

Pertusaria communis β variolosa contains *orbiculatic acid*, $C_{22}H_{36}O_7$, crystallising in colourless leaflets melting at 82°; it is monobasic, and does not give a coloration with ferric chloride. K. J. P. O.

Action of Bromoacetophenone on Sodioacetylacetone. By Fr. March (*Compt. rend.*, 1901, 133, 45—47).—A triketone *benzoyldiacetylethane*, $CH(COMe)_2{\cdot}CH_2{\cdot}COPh$, is obtained by the action of bromoacetophenone on sodioacetylacetone in presence of alcohol, and is separated by means of a compound, $C_{26}H_{26}O_6Cu$, which it forms with cupric acetate, and which can be crystallised from chloroform, although it is not very soluble in other organic solvents. This compound melts and decomposes at 219—220°, and is decomposed by sulphuric acid with liberation of the triketone. The triketone forms colourless crystals which melt at 57—58°, and dissolve in most ordinary organic solvents except light petroleum. When treated with alcoholic potash, the triketone yields acetic acid and the acetophenoneacetone described by Paal; with semicarbazide hydrochloride, it yields a compound, $C_{14}H_{15}O_2N_3$, forming small needles which melt and decompose at 262—264°; this is under investigation. With phenylhydrazine, the triketone yields a red oil which crystallises with difficulty; it has the composition $C_{19}H_{18}ON_2$, and melts at 87—88°. C. H. B.

Derivatives of *o*-Benzoquinone. By C. LORING JACKSON and WALDEMAR KOCH (*Amer. Chem. J.*, 1901, **26**, 10—46).—When the lead salt of quinol is treated with an alcoholic solution of iodine, quinone is produced. Similarly, if the lead salt of catechol is shaken with a solution of iodine in chloroform, a garnet-red solution of *o*-quinone is obtained, which possesses no odour except that of the chloroform. If this solution is left for 24—30 hours, the *o*-quinone is completely converted into *o*-dihydroxyphenylhydroxy-*o*-quinone, which separates as a black precipitate; all attempts to isolate *o*-quinone from the solution resulted in the formation of the same substance.

o-*Dihydroxyphenylhydroxy*-o-*quinone*, $C_6H_3(OH)_2\cdot C_6H_2O_2\cdot OH$, forms a nearly black, amorphous powder, which does not melt but decomposes gradually above 170°, and is readily soluble in alcohol, ether, or glacial acetic acid; it yields a black, *lead* salt. This compound has also been obtained by Torrey and one of the authors by the electrolytic oxidation of catechol. On reduction with sodium amalgam, a black substance is formed, but catechol is not produced. The *tribenzoyl* derivative is obtained as a light yellow, amorphous powder, which is readily soluble in chloroform. By the action of phenylhydrazine on *o*-dihydroxyphenylhydroxy-*o*-quinone, a golden-yellow *substance* is produced containing 6·39 per cent. of nitrogen, whilst by the action of the same reagent on the tribenzoyl derivative, a *substance* containing 4·42 per cent. of nitrogen is obtained.

When dry hydrogen chloride is passed into a freshly prepared chloroform solution of *o*-quinone, *chlorocatechol*, $C_6H_3Cl(OH)_2$, is produced, which crystallises in white, pearly plates, and is readily soluble in water, alcohol, ether, benzene, chloroform, or acetone; its *lead* salt was prepared and analysed. When the solution of *o*-quinone is treated with ammonium sulphide or sulphur dioxide, catechol is produced, whilst by the action of bromine tetrabromocatechol is formed. If the *o*-quinone solution is added drop by drop to a solution of benzenesulphinic acid in chloroform, o-*dihydroxydiphenylsulphone*, $SO_2Ph\cdot C_6H_3(OH)_2$, is produced, which crystallises in short, thick, white prisms, melts at 153°, dissolves readily in alcohol, ether, chloroform, or glacial acetic acid, and is apparently not identical with the compound obtained by Hinsberg and Himmelschein (Abstr., 1896, i, 685) by the oxidation of catechol in presence of benzenesulphinic acid. By the action of aniline on the chloroform solution of *o*-quinone, dianilinoquinoneanilide is formed, identical with the compound prepared by Zincke and Hagen (Abstr., 1885, 787) by the action of aniline and glacial acetic acid on *p*-quinone. When the solution of *o*-quinone is treated with *o*-phenylenediamine, a phenazine is not produced, but the diamine suffers oxidation.

When tetrabromo-*o*-quinone is heated with acetic acid, it is partially converted into *hexabromo*-o-*quinocatechol ether*, $C_{12}O_4Br_6$, which is obtained as a red precipitate, does not melt, and is soluble in all the common solvents; it crystallises from warm nitrobenzene in short, slender, vermilion-red prisms, but undergoes decomposition if the solution is heated above 100°. This substance is more readily prepared by heating a solution of tetrabromo-*o*-quinone and tetrabromocatechol in acetic acid; if ether or chloroform is used as the solvent, no reaction takes place (compare Zincke, Abstr., 1887, 808). On reduction with sodium amalgam in an atmosphere of carbon dioxide, a purplish-white product is obtained together with a small proportion of catechol; when the purplish-white substance is treated with nitric acid, hexabromo-*o*-quinocatechol ether is regenerated, and may be again reduced with sodium amalgam; by repeating these alternate oxidations and reductions, the compound may be completely converted into catechol. The purplish-white compound is probably *hexabromo*-o-*dihydroxycatechol ether*, $C_{12}Br_6O_2(OH)_2$; it crystallises from nitrobenzene in small, chocolate-brown needles, and does not melt below 300°. Hexabromo-*o*-quinocatechol ether is not decomposed when boiled with strong sulphuric acid, but if heated with concentrated hydrochloric acid at 160—175° in a sealed tube, it is converted into the purplish-white compound described above.

When tetrabromo-*o*-quinone is heated with tetrabromoquinol, bromoanil and tetrabromocatechol are formed; tribromopyrogallol reacts with it in a similar manner, with production of tetrabromocatechol, hexabromo-*o*-quinocatechol ether, and its purplish-white reduction product. If tetrabromo-*o*-quinone and tribromoresorcinol are allowed to react in acetic acid solution, a pink precipitate of *ditribromo*-m-*hydroxyphenyldibromo*-o-*quinophenylene ether*, $C_6Br_2O_2[C_6Br_3(OH)_2]_2$, is formed, which crystallises from benzene in slender, lemon-yellow prisms with square ends, melts at 217°, and is soluble in ether, alcohol, or chloroform, but does not dissolve in sodium hydroxide.

When tetrabromo-*o*-quinone is heated with glacial acetic acid, a white *substance*, $C_{14}H_2O_5Br_8$, is produced, which may be separated from the hexabromo-*o*-quinocatechol ether simultaneously formed by extraction with hot alcohol, in which the latter is insoluble; it crystallises from glacial acetic acid in small, rhombic plates with a pearly lustre, is easily soluble in ether, benzene, chloroform, acetone, or ethyl acetate, and is extremely stable.

Ethyl acetate reacts with tetrabromo-*o*-quinone, with formation of tetrabromocatechol and hexabromo-*o*-quinocatechol ether. E. G.

Thymoquinone and Thymoquinol in Wild Bergamot Oil. By I. W. Brandel and Edward Kremers (*Pharm. Review*, 1901, 19, 200—203 and 244—246).—The oil of *Monarda fistulosa* contains, in addition to cymene, thymol, and *d*-limonene, small quantities of thymoquinone and thymoquinol; the dark colour of the oil, and the colour produced in both its phenolic and non-phenolic portions on keeping, are probably due to the production of the highly coloured thymoquinhydrone. W. A. D.

Electrolytic Reduction of *o*-Nitroanthraquinone to *o*-Aminoanthraquinone. By Joh. Möller (*Zeit. Elektrochem.*, 1901, 7, 741—743).—A solution of *o*-nitroanthraquinone (1 gram) in alcohol (270 grams) and concentrated sulphuric acid (30 grams) served as cathode solution in a cell with a diaphragm and platinum electrodes.

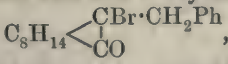
The anode solution was dilute sulphuric acid, temperature 50°, and current density 0·001 ampere per sq. cm. The yield of *o*-aminoanthraquinone was 70 per cent. of the theoretical quantity. T. E.

Action of Benzaldehyde on Sodiomenthol. New Methods of preparing Benzylidenementhone. By CAMILLE MARTINE (*Compt. rend.*, 1901, **133**, 41—43).—The action of benzaldehyde on sodiomenthol yields an oil boiling at 182—185° under 10 mm. pressure, and when this is heated with alcoholic potash, it yields potassium benzoate, menthol, benzyl alcohol, and a liquid boiling at 195—196° under 15 mm. pressure. The last, when treated with hydrobromic acid in presence of acetic acid, yields benzylidenementhone hydrobromide, which forms silky needles melting at 115°. When treated with sodium ethoxide, it is converted into benzylidenementhone, which has $[\alpha]_D$ +22·8° to +24·3°. The benzylidenementhone obtained according to Wallach's method by the action of hydrogen chloride on menthone and benzaldehyde, has the same rotatory power whether the original menthone is dextro- or lævo-gyrate. Similarly, the action of benzaldehyde on either *d*- or *l*-sodiomenthone yields the same *d*-benzylidenementhone. There is, however, evidence that a *l*-benzylidenementhone is formed at the same time in both cases, with an equal but opposite rotatory power, but forming no hydrobromide and no crystallisable oxime. It is clear that sodiomenthol behaves like sodioborneol in contact with benzaldehyde. The by-products obtained by the action of alcoholic potash indicate that the reaction takes place in the manner suggested by Claisen (Abstr., 1887, 574). C. H. B.

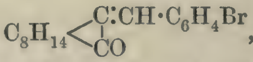
***cyclo*Citral Semicarbazone.** By R. SCHMIDT (*Ber.*, 1901, **34**, 2451).—The fact that *β-cyclo*citral is quantitatively regenerated from its semicarbazone by acids (*Ber.*, 1900, **33**, 3721) is remarkable, since with the semicarbazones of aliphatic and hydroaromatic aldehydes more complex decomposition usually occurs, although with those of ketones a good yield of the ketone is usually obtained.

W. A. D.

New Derivatives of Benzylcamphor and Benzylidenecamphor. By ALBIN HALLER and JULES MINGUIN (*Compt. rend.*, 1901, **133**, 79—84. Compare Abstr., 1900, i, 452).—*Phenylbromohomocampholic acid*, $CHPhBr\cdot CH_2\cdot C_8H_{14}\cdot CO_2H$, prepared by treating benzylidenecampholic acid (*loc. cit.*) with a solution of hydrogen bromide in glacial acetic acid, forms hard, white crystals melting at 135°, and when dissolved in toluene has $[\alpha]_D$ +44°8′. When heated at 100° with a solution of hydrogen bromide in acetic acid, phenylhydroxyhomocampholic acid is formed; with alcoholic potash, it yields a mixture of the last-mentioned acid and benzylidenecampholic acid.

Benzylbromocamphor,  $C_8H_{14}\Big<\begin{array}{l}CBr\cdot CH_2Ph\\ \mid\\ CO\end{array}$, prepared by heating a solution of benzylcamphor in carbon disulphide with bromine, crystallises in large prisms belonging to the orthorhombic system, melts at 94—95°, and has $[\alpha]_D$ +61° in alcoholic solution. With alcoholic potash, it yields benzylidenecamphor, and thus differs markedly in its behaviour from the isomeric bromobenzylcamphor (*loc. cit.*). By the action of heat alone, hydrogen bromide is eliminated with the formation of benzylidenecamphor. Hydrobromic acid has no action at 100°; when reduced with zinc and hydrochloric acid, benzylcamphor is regenerated. A second stereoisomeric *benzylbromocamphor* is also produced in the bromination of benzylcamphor in the manner just described, and forms crystals which melt at 90—91°, and have, when dissolved in alcohol, $[\alpha]_D$ +20°. Towards heat and alcoholic potash, it behaves in the same manner as its stereoisomeride.

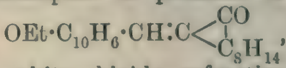
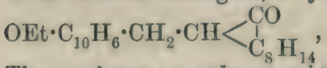
When the viscous product obtained on brominating benzylcamphor with excess of bromine is boiled with alcoholic potash, a mixture of *o*- and *p*-bromobenzylidenecamphor is obtained, which is separated by fractional crystallisation from alcohol, in which the para-compound is the less soluble.

p-*Bromobenzylidenecamphor*,  $C_8H_{14}\left<\begin{array}{l}C{:}CH\cdot C_6H_4Br\\ |\\ CO\end{array}\right.$, crystallises in orthorhombic prisms, melts at 129—130°, and, when dissolved in toluene, has $[\alpha]_D$ +315°. The *ortho*-derivative crystallises in monoclinic prisms, melts at 105°, and, when dissolved in toluene, has $[\alpha]_D$ +283°. On oxidation with potassium permanganate, they yield respectively *p*- and *o*-benzoic acid together with camphoric acid.

p-*Bromophenylhydroxyhomocampholic acid*,

$$C_6H_4Br\cdot CH(OH)\cdot CH_2\cdot C_8H_{14}\cdot CO_2H,$$

prepared by treating *p*-bromobenzylidenecamphor with a saturated solution of hydrogen bromide in acetic acid, and then boiling the additive product thus formed with alcoholic potash or hydrogen bromide in acetic acid, forms crystals which melt at 100°, and, when dissolved in toluene, have $[\alpha]_D$ +57°3′. K. J. P. O.

Combination of Camphor with β-Hydroxy-α-naphthaldehyde. By ANDRÉ HELBRONNER (*Compt. rend.*, 1901, **133**, 43—45).—The action of the β-ethoxy-α-naphthaldehyde on sodiocamphor in presence of toluene yields *ethoxynaphthylidenecamphor*,  $OEt\cdot C_{10}H_6\cdot CH{:}C\left<\begin{array}{l}CO\\ |\\ C_8H_{14}\end{array}\right.$, which separates from alcohol in brilliant, white, highly refractive crystals of the hexagonal system. It melts at 100°, and has $[\alpha]_D$ +121·13° in a 5·32 per cent. alcoholic solution. With sulphuric acid, it gives a blood red coloration, which disappears if water is added. With sodium amalgam, it yields the corresponding hydro-derivative,  $OEt\cdot C_{10}H_6\cdot CH_2\cdot CH\left<\begin{array}{l}CO\\ |\\ C_8H_{14}\end{array}\right.$, which melts at 112°, and has $[\alpha]_D$ +52·8°. The analogous *methoxynaphthylidenecamphor* crystallises in hexagonal forms, melts at 78°, and has $[\alpha]_D$ +119·86°, whilst its reduction product melts at 96° and has $[\alpha]_D$ 57·8°. C. H. B.

Phellandrene Nitrite and Oils containing Phellandrene. By OSWALD SCHREINER (*Pharm. Arch.*, 1901, **4**, 90—95).—Crude phellandrene nitrite, prepared from a eucalyptus oil containing phellandrene, has $[\alpha]_D$ +28·5°, but can be resolved by fractional crystallisation from ethyl acetate and methyl alcohol into two components of different optical activity. One of these melts at 120—121°, has $[\alpha]_D$ +123·5°, and forms long, well-defined needles, whilst the other melts at 100—101°, has $[\alpha]_D$ $-36°$, and crystallises in confused aggregates. The melting point of the latter changes to 105—106° on crystallisation from methyl alcohol, so that evidently it does not correspond with a definite compound. The highest melting point hitherto given for phellandrene nitrite is 105° (Wallach and Herbig, Abstr., 1896, i, 101), the pure substance probably never having been obtained; as a consequence, all previous diagnoses of the presence of phellandrene in many ethereal oils, based on the formation of a nitrite melting at about 105°, are inexact. W. A. D.

Conversion of Thujylamine into Thujene. By L. Tschugaeff (*Ber.*, 1901, **34**, 2276—2281).—The dry distillation of thujylamine hydrochloride gives *iso*thujene and not thujene, which might have been expected as the first product of the action. *Trimethylthujylammonium iodide*, $C_{10}H_{17}Me_3NI$, prepared by the action of methyl iodide and potassium hydroxide on thujylamine, crystallises from a mixture of chloroform and methyl alcohol in long, prismatic crystals, has $[\alpha]_D$ $+42·61°$ in chloroform solution, and is only sparingly soluble in cold water. The *base*, $C_{10}H_{17}Me_3N·OH$, mixed with carbonate, was obtained as a crystalline mass, and was decomposed by dry distillation. The product consisted of thujene, which boils at 151—153°, has a sp. gr. 0·8263 at 20°/4°, n_D 1·45022 at 20°, and $[\alpha]_D$ $-8·23°$; these constants are entirely different from those of Wallach's *iso*thujene, but agree closely with those of the thujene prepared from thujyl alcohol through the xanthate (this vol., i, 38). The rotatory power is, however, nearly twice as great as that of the thujene from thujyl alcohol, and it is suggested that two stereoisomeric alcohols are perhaps formed by the reduction of thujone, and that these give rise to two stereoisomeric thujenes; by collecting the last fraction in the distillation of methyl thujylxanthate, a dextrorotatory thujene was obtained which has α_D $+21·83°$ in a 10 cm. tube. *Dimethylthujylamine*, $C_{10}H_{17}NMe_2$, formed as a by-product in the preparation of trimethylthujylamine iodide, is a liquid boiling at 213·5—214°, has a sp. gr. 0·8606 at 20°/4°, and $[\alpha]_D$ $+141·76°$; the *hydrochloride* is very readily soluble in water and alcohol, but the *nitrate* is only sparingly so and crystallises readily; the *platinichloride* separates from hot alcohol as an orange-red, crystalline powder. T. M. L.

Oil of Jasmine-blossoms. By Ernst Erdmann (*Ber.*, 1901, **34**, 2281—2283. Compare Hesse, Abstr., 1900, i, 454; this vol., i, 220).—In reply to Hesse, it is urged that it is very unlikely that large amounts of scent are produced during enfleurage, and the difference in yield by enfleurage and by extraction with light petroleum is explained as due merely to a difference in conditions. T. M. L.

Oil of Neroli. By Ernst Erdmann and Hugo Erdmann (*Ber.*, 1901, **34**, 2283).—A question of priority (compare Walbaum, this vol., i, 39). T. M. L.

Formation of Resin in several Abietes. By Alexander Tschirch and E. Faber (*Arch. Pharm.*, 1901, **239**, 249—257).—The authors discuss the question of the origin of resin and the part played by the bark in its formation. K. J. P. O.

Robinin and Rutin. By ERNST SCHMIDT (*Chem. Centr.*, 1901, ii, 121; from *Apoth.-Zeit.*, 16, 357—358. Compare Perkin, Proc., 1901, 17, 87—88).—By the decomposition of robinin, rhamnose and a yellow dye are formed. The latter, $C_{15}H_{10}O_6$, crystallises from hot water in slender needles, and is very similar to Tschirch and Polacco's rhamnolutin. It is easily attacked by dilute potassium hydroxide solution, and forms an acetyl derivative, $C_{15}H_6O_2(OAc)_4$, which separates in colourless crystals and melts at 182—183°. The ethyl derivative crystallises in yellow needles. The mother liquor of robinin contains asparagine and sugar.

[With WALJASCHKO.]—Rutin, prepared from *Ruta graveolens*, when hydrolysed, forms rhamnose, dextrose, and quercetin, the last being identical with that prepared from quercitrin. The rutin obtained from common rue is not identical with robinin or quercetin, but resembles the rutin isolated from capers, and also that from *Viola tricolor* (Mandelin and Wachs). E. W. W.

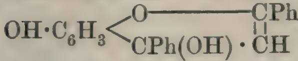
Uganda Aloes. By ALEXANDER TSCHIRCH and J. KLAVENESS (*Arch. Pharm.*, 1901, 239, 241—257. Compare this vol. i, 399).—Uganda aloes, on distillation with 1 per cent. potassium carbonate solution, yield a small quantity of an ethereal oil which has an odour of roses and solidifies. By Léger's method (*Bull. Soc. Chim.*, 1900, [iii], 23, 790), *uganda-aloin*, $OMe\cdot C_{15}H_{11}O_4(OH)_2$, was obtained, and is identical with capaloin (m. p. 138—139°) prepared from Cape aloes by Léger (*loc. cit.*). The *dibenzoyl* derivative forms a pale yellow powder melting at 107—108°. With chlorine and bromine, uganda-aloin gives crystalline compounds, and with hydrochloric acid a black powder (alonigrin). On oxidation with nitric acid, chrysaminic, picric, and oxalic acids are produced.

The resin from Uganda aloes consists of uganda-aloresinotannol *p*-coumarate, which is identical with or nearly related to the ester found in Natal aloes. Emodin is also present, and can be isolated by extracting Uganda aloes with acetone, and precipitating the resin with ether, or by extracting with ether the acid mother liquor from the preparation of the resin. K. J. P. O.

Later Developments of the Chemistry of the Anthracene Dyes. By A. BUNTROCK (*Ber.*, 1901, 34, 2344—2349).—A reply to and criticism of papers by Liebermann (see this vol., i, 478).

R. H. P.

Bilirubin, the Red Colouring Matter of the Bile. By WILLIAM R. ORNDORFF and J. E. TEEPLE (*Amer. Chem. J.*, 1901, 26, 86—92).—The average of a large number of analyses of bilirubin, obtained from ox gall-stones and crystallised from dimethylaniline, indicates the formula $C_{34}H_{36}O_7N_4$; it contains no alkyloxy-groups, but has one alkyl group attached to nitrogen, and is probably a pyrrole derivative. E. G.

Derivatives of 1 : 4-Benzopyranol, the Parent Substance of a New Class of Colouring Matters. III. By Carl Bülow and Walther von Sicherer (*Ber.*, 1901, 34, 2368—2385. Compare this vol., i, 400, 559).—The 1 : 3-diketone, dibenzoylmethane, condenses with resorcinol to form 7-*hydroxy*-2 : 4-*diphenyl*-1 : 4-*benzopyranol*,  $OH\cdot C_6H_3 < \begin{matrix} O\text{———}CPh \\ \Vert \\ CPh(OH)\cdot CH \end{matrix}$, in which the hydroxyl group in position 4 remains intact (compare *loc. cit.*) and exhibits carbinolic rather than phenolic properties. The *hydrochloride*, $C_{21}H_{16}O_3,HCl,2H_2O$, is obtained by the condensation of resorcinol with dibenzoylmethane in acetic acid solution in the presence of hydrogen chloride, and crystallises in large, yellowish-orange or orange needles, which begin to decompose about 200° and give an intense yellow-green fluorescence when dissolved in sulphuric acid. The colour *base* crystallises in ruby-red needles decomposing at 250—260°.

When the hydrochloride is distilled with 10 per cent. potassium hydroxide, acetophenone passes over and benzoresorcinol is found in the alkaline liquor together with a small quantity of benzoic acid, arising from the decomposition of the last-mentioned substance.

7-*Hydroxy*-2 : 4-*diphenyl*-1 : 4-*benzopyranol sulphate*,

$$C_{21}H_{16}O_3,H_2SO_4,2H_2O,$$

prepared from the hydrochloride and alcoholic sulphuric acid, crystallises in orange-red needles; the *picrate* forms yellow needles darkening at 200° and decomposing at 260°; the *platinichloride*, lemon-yellow, insoluble needles decomposing suddenly at 235°; the *aurichloride*, canary-yellow plates melting and decomposing at 236°.

The *diacetyl* derivative of the benzopyranol, prepared from the hydrochloride and acetic anhydride, crystallises in red needles melting and decomposing at 110—112°, fluoresces with concentrated sulphuric acid, and is insoluble in alkalis. The *monoacetyl* derivative is formed when the diacetyl compound is heated with boiling dilute sulphuric acid, and crystallises in red needles melting at 119°, and easily soluble in alkalis; the monoacetyl compound is readily benzoylated by the Schotten-Baumann method.

The *dibenzoyl* derivative, prepared from the hydrochloride, forms ruby-red, prismatic crystals decomposing slowly at 110°.

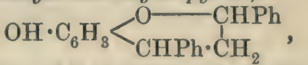
The *dimethyl ether*, prepared from methyl iodide and the sodium derivative of the benzopyranol, crystallises in white needles melting at 104° and dissolves in concentrated sulphuric acid, forming a colourless solution which exhibits a fine yellowish-green fluorescence.

2 : 3-*Dibromo*-7-*hydroxy*-2 : 4-*diphenyl*-1 : 4-*benzopyranol*, $C_{21}H_{16}O_3Br_2$, prepared by the action of bromine on an acetic acid solution of the hydrochloride, is an additive compound crystallising in reddish-brown spikes, decomposing at 240°, and easily soluble in dilute alkalis; its solution in sulphuric acid is not fluorescent; by zinc dust and acetic acid, it is converted into a colourless substance which does not contain bromine.

8-*Nitroso*-7-*hydroxy*-2 : 4-*diphenyl*-1 : 4-*benzopyranol*, $C_{21}H_{15}O_3\cdot NO$, crystallises in scarlet needles softening at 135° and melting at 158°.

By the action of hydrochloric acid under pressure on the hydrochloride, a *substance*, $C_{21}H_{15}O_2Cl,HCl$, is obtained which crystallises in yellow spikes, decomposing slowly at 140—170°, and losing hydrogen chloride on exposure to air. The authors regard this substance as the hydrochloride of a chloro-derivative of the benzopyranol, in which chlorine has replaced the carbinolic hydroxyl.

7-*Hydroxy*-2 : 4-*diphenylbenzodihydropyran*,



$$OH\cdot C_6H_3<\begin{matrix}O\text{———}CHPh\\ CHPh\cdot CH_2\end{matrix},$$

prepared by long boiling of the acetic acid solution of the hydrochloride of the benzopyranol with zinc dust, forms a white, amorphous powder, which becomes red at 142° and above 150° decomposes; it dissolves in alkalis, does not fluoresce with sulphuric acid, and is oxidised to the benzopyranol by mercuric oxide, &c.

If in the reduction the boiling is stopped as soon as the solution becomes colourless, the liquid contains a substance, which oxidises most readily in the air, and is probably the leuco-base, the carbinolic hydroxyl group having been replaced by hydrogen. The *acetyl* derivative of the benzodihydropyran, $C_{21}H_{17}O_2Ac$, forms a yellowish, amorphous powder melting at 112—115°. K. J. P. O.

Dinaphthoxanthones. By R. Fosse (*Compt. rend.*, 1901, **133**, 100—102).—*Bromodinaphthoxanthone*, $CHBr<\begin{matrix}C_{10}H_6\\ C_{10}H_6\end{matrix}>O$, prepared by the action of bromine on a solution of dinaphthoxanthone in bromoform, crystallises in red prisms (green by reflected light) and melts at 218—220°. It is soluble in moderately diluted, but not in concentrated acids. From the solution in hydrobromic acid, a hydrated hydrobromide crystallises in golden-red needles. With alcohol, this bromo-derivative reacts, yielding aldehyde, hydrogen bromide, and dinaphthoxanthone.

Bisdinaphthoxanthoneamine, $NH\cdot[CH{:}(C_{10}H_6)_2{:}O]_2$, prepared from the bromo-derivative and alcoholic or aqueous ammonia, forms lustrous crystals melting and decomposing at 230°. With hydrobromic acid, the amine becomes blood-red and decomposes into ammonium bromide and bromodinaphthoxanthone; with hydrochloric acid, into ammonium chloride and chlorodinaphthoxanthone.

Chlorodinaphthoxanthone, $CHCl{:}(C_{10}H_6)_2{:}O$, prepared by the action of chlorine on dinaphthoxanthone, crystallises in red needles melting at 150°. It resembles the bromo-derivative in properties, and forms compounds with mercuric chloride or bromide and with platinic chloride. K. J. P. O.

Action of Vegetable Alkaloids on certain Indicators. By A. Astruc (*Compt. rend.*, 1901, **133**, 98—100).—Solutions of various alkaloids in water, absolute alcohol, amyl alcohol, or benzene were titrated with hydrochloric acid in the presence of the indicators helianthin A, rosolic acid, and phenolphthalein.

Of the alkaloids derived from pyridine, those containing a piperidine nucleus are stronger bases than those containing only the unreduced pyridine nucleus. Thus, conicine, conhydrine, and sparteine act on the three indicators in aqueous solution, whilst nicotine and pilocarpine (alkaloids derived from pyridine) do not affect phenolphthalein; in a neutral medium, the former have an action on helianthin A and rosolic acid, the latter only on helianthin A. Sparteine possesses two basicities; in aqueous solution, in the presence of helianthin A, it requires 2 mols. of hydrogen chloride, but in the presence of rosolic acid or phenolphthalein, it requires only 1 mol. of the acid for neutralisation. Further, in a neutral solvent, sparteine behaves as a univalent base towards rosolic acid. These facts show that sparteine possesses one piperidine and no pyridine nucleus.

Of the alkaloids derived from trapanine, trapanine, atropine, and hyoscyamine in aqueous solution are strong bases, and behave towards indicators as does piperidine. In benzene solution, trapanine is basic towards rosolic acid, whilst atropine and hyoscyamine are neutral. Ecgonine and benzoylecgonine are without action on indicators in aqueous solution; in benzene, they are neutral to rosolic acid, univalent bases in presence of helianthin A, and univalent acids in presence of phenolphthalein.

The alkaloids derived from quinoline (quinine, cinchonine, cinchonidine, &c.) have two basicities; in aqueous solution, they are neutral to phenolphthalein, require 1 mol. of hydrogen chloride in presence of rosolic acid, and 2 mols. in presence of helianthin A. In benzene, quinine acts only on the last-mentioned indicator, and is bivalent.

Of the alkaloids derived from oxazine and *iso*quinoline (in which class are included the alkaloids from opium) codeine, morphine, and thebaine, when dissolved in water or dilute alcohol, can be approximately titrated in the presence of rosolic acid, whilst papaverine, narceine, and narcotine are neutral to this indicator; all are univalent bases towards helianthin A. In benzene solution, they all affect the last-mentioned indicator; morphine and narceine in this solvent can respectively be titrated approximately by potassium hydroxide in the presence of phenolphthalein.

Aconitine, veratrine, strychnine, and brucine only act as feeble bases on helianthin A.

Of the purine group of bases, hydrated caffeine is neutral to all indicators; a solution of the anhydrous base in benzene affects methyl-orange, but cannot be titrated in the presence of this indicator.

It is pointed out that there is a complete parallelism between the thermochemistry of these bases and their behaviour towards indicators.

K. J. P. O.

Relation of Hyoscyamine to Atropine and of Scopolamine to *i*-Scopolamine. By JOHANNES GADAMER (*Arch. Pharm.*, 1901, **239**, 294—336. Compare Abstr., 1900, i, 91).—By the action of water at the ordinary temperature, hyoscyamine is hydrolysed to *l*-tropic acid and *i*-tropine, whilst by alkalis this base is converted into atropine (*i*-tropine *r*-tropate), and at the same time partially hydrolysed. The change of hyoscyamine into atropine then is a conversion of lævorotatory tropic acid into racemoid tropic acid. Addition of tropine to an aqueous solution of hyoscyamine hastens the hydrolysis, and, at the same time, effects a certain amount of conversion into atropine, which in its turn is to a small extent hydrolysed. In alcoholic solution, hyoscyamine is slowly transformed into atropine, a change which is hastened by addition of tropine.

The conversion of hyoscyamine into atropine is best effected as follows. A solution of the base (1 gram) in absolute alcohol (15 grams), to which sodium hydroxide (0·03 gram) has been added, is allowed to remain at 5° until it is inactive (about 24 hours). Carbon dioxide is passed in, the filtered solution evaporated under reduced pressure, and water added to precipitate the atropine.

Scopolamine (*i*-scopoline *l*-tropate) in a similar manner is converted by alkalis into *i*-scopolamine (that is, Hesse's atroscine, *i*-scopoline *r*-tropate) and also partially hydrolysed into scopoline and *l*-tropic acid. In absolute alcohol, no change takes place until tropine is added.

The existence of these changes explains the fact that in young roots of *Belladonna* only hyoscyamine is present, whilst in old roots atropine is found as well.

The author finds that scopolamine in alcoholic solution has $[\alpha]_D$ $-18°$ at 20° and in aqueous solution $-28°$; the hydrobromide has $[\alpha]_D$ $-15·72°$ in alcoholic solution. Pure *l*-tropic acid, prepared by hydrolysis of scopolamine in aqueous solution, crystallises from water in needles melting at 125—126°, and has $[\alpha]_D$ $-71·81°$. Alkalis have no effect on the rotation of the pure acid.

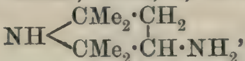
Inactive atropine, prepared in a completely pure state by the method previously described, melts at 115—116°, and when pulverised at 112—113°. The sulphate, when carefully dried over sulphuric acid, melts at 187—188°, but traces of moisture greatly depress the melting point. The author believes that the surest means of testing atropine sulphate for the presence of hyoscyamine is by use of the polarimeter.
K. J. P. O.

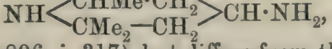
Stereochemistry of the Piperidine Series. II. By W. Hohenemser and Richard Wolffenstein (*Ber.*, 1901, **34**, 2420—2423. Compare Abstr., 1899, i, 936).—The same laws connecting structure and specific rotatory power as were established in the former paper hold for the following alkyl derivatives of coniine; these bases were prepared by heating coniine with solid potassium hydroxide and a slight excess of the alkyl bromide for 14 hours at 170°. 1-*Ethylconiine* boils at 187—188° under 755 mm. pressure, and has a sp. gr. 0·8398 at 21°, $[\alpha]_D$ 75·62° and $[M]_D$ 117·21; the *hydrochloride* melts at 111°, the *hydrobromide* at 163°, the *platinichloride* at 110—111°, the *aurichloride* at 85—86°, whilst the *mercurichloride* and *picrate* are oils. 1-*Propylconiine* boils at 207—208° under 764·3 mm. pressure, and has a sp. gr. 0·8423 at 18°, $[\alpha]_D$ 76·21°, $[M]_D$ 128·80; the *hydrochloride* melts at 144°, the *hydrobromide* at 186°, the *platinichloride* at 172—173°, the *aurichloride* at 103—104°, and the picrate at 60°; the *mercurichloride* is an oil.

1-iso*Amylconiine* boils at 238—240° under 773·4 mm. pressure, and has a sp. gr. 0·8352 at 23·5°, $[\alpha]_D$ 75·14°, $[M]_D$ 148·02; the *hydrochloride* is deliquescent, the *hydrobromide* melts at 132·5°, the *aurichloride* at 97—98°, and the *picrate* at 66·5°; the *platinichloride* and *mercurichloride* are oils.

The foregoing active bases could not be purified by conversion into the *d*-tartrates, owing to these salts not crystallising well; the rotatory powers given apply to bases which were isolated directly, and are most probably correct, since on heating these substances with solid potassium hydroxide for 14 hours at 170°, no change of rotatory power occurs. W. A. D.

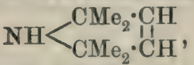
New Alkaloid from the Elder Tree. By F. Malméjac (*J Pharm.*, 1901, [vi], 14, 17—19).—See this vol., ii, 572.

Aminopyrrolidines. By Hermann Pauly and A. Schaum (*Ber.*, 1901, 34, 2287—2289. Compare Pauly and Rossbach, Abstr., 1899, i, 773, and Pauly and Boehm, Abstr., 1900, i, 357).—3-Amino-2 : 2 : 5 : 5-tetramethylpyrrolidine,  $\mathrm{NH}<\begin{array}{l}\mathrm{CMe_2\cdot CH_2}\\ \mathrm{CMe_2\cdot CH\cdot NH_2}\end{array}$, very closely resembles the two stereoisomeric *p*-aminotrimethylpiperidines,

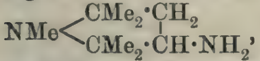


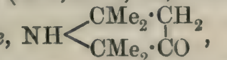
$$\mathrm{NH}<\begin{array}{l}\mathrm{CHMe\cdot CH_2}\\ \mathrm{CMe_2{-}CH_2}\end{array}>\mathrm{CH\cdot NH_2},$$

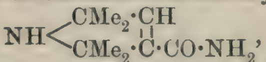
of Harries (Abstr., 1896, i, 317), but differs from them in that nitrous acid does not convert it into the corresponding hydroxy-compound, but gives the unsaturated 2 : 2 : 5 : 5-*tetramethylpyrroline*,



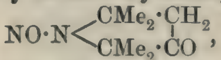
$$\mathrm{NH}<\begin{array}{l}\mathrm{CMe_2\cdot CH}\\ \mathrm{CMe_2\cdot CH}\end{array},$$

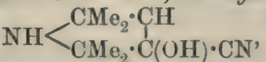
which is a mobile liquid and boils at 114—116°. It also resembles Harries' α-compound in that it gives two isomeric *thiocarbamates* melting at 142—144° and 170° respectively. The 1-*methyl* derivative,  $\mathrm{NMe}<\begin{array}{l}\mathrm{CMe_2\cdot CH_2}\\ \mathrm{CMe_2\cdot CH\cdot NH_2}\end{array}$, is an ice-like mass which melts at 40°, boils at 190°, and also gives two *thiocarbamates* melting at 103° and 172° respectively. T. M. L.

3-Keto-2 : 2 : 5 : 5-tetramethylpyrrolidine. By Hermann Pauly and Carl Boehm (*Ber.*, 1901, 34, 2289—2291).—3-*Keto*-2 : 2 : 5 : 5-*tetramethylpyrrolidine*,  $\mathrm{NH}<\begin{array}{l}\mathrm{CMe_2\cdot CH_2}\\ \mathrm{CMe_2\cdot CO}\end{array}$, prepared by the action of potassium hypobromite on carbaminotetramethylpyrroline,



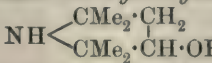
$$\mathrm{NH}<\begin{array}{l}\mathrm{CMe_2\cdot CH}\\ \mathrm{CMe_2\cdot C\cdot CO\cdot NH_2}\end{array},$$

is a mobile liquid readily volatile in a current of steam; it boils at 175°, and as a ketonic secondary amine very closely resembles triacetonamine. The *nitrosoamine*,  $\mathrm{NO\cdot N}<\begin{array}{l}\mathrm{CMe_2\cdot CH_2}\\ \mathrm{CMe_2\cdot CO}\end{array}$, forms yellow felted needles, and melts at 75·5—76°; the *cyanohydrin*,



$$\mathrm{NH}<\begin{array}{l}\mathrm{CMe_2\cdot CH}\\ \mathrm{CMe_2\cdot C(OH)\cdot CN}\end{array},$$

forms minute tablets, melts at 138°, and is readily decomposed; the *oxime* crystallises in tablets or prisms, melts at 172° and is reduced by sodium and alcohol to 3-aminotetramethylpyrrolidine. Sodium amalgam reduces the ketone to 3-*hydroxytetramethylpyrrolidine*,



$$\mathrm{NH}<\begin{array}{l}\mathrm{CMe_2\cdot CH_2}\\ \mathrm{CMe_2\cdot CH\cdot OH}\end{array},$$

which forms square tablets, melts at 71°, and boils at 90—91° under 11·5 mm. pressure; a *base*, $C_8H_{19}ON$, is also produced by further reduction; it crystallises in prisms, melts at 26°, boils at 87·8—88° under 11·5 mm. pressure, and is separated from the preceding compound by means of the difference in solubility of the hydrochlorides in acetone. The *benzoate* of *p*-hydroxytetramethylpyrrolidine is a powerful local anæsthetic. T. M. L.

Stereochemistry in the Piperidine Series. II. By ARTHUR MARCUSE and RICHARD WOLFFENSTEIN (*Ber.*, 1901, **34**, 2426—2430).—Lupetidine and *iso*lupetidine (2 : 6-dimethylpiperidines; Abstr., 1899, i, 937), differ notably in their behaviour with acid chlorides; with benzenesulphonic chloride, the former interacts only slowly and under special conditions, whilst the latter acts rapidly and completely, although with benzoyl chloride the converse is true. With phenylcarbimide and phenylthiocarbimide, however, the action of the two bases is the same. That the difference of action is due to the different influences on the imino-group of the two adjacent methyl radicles occupying respectively a *cis*- and *trans*-position, is shown by the fact that the two isomeric forms of copellidine (2-methyl-5-ethylpiperidine) interact with all the foregoing substances with equal ease.

Lupetidine does not combine with benzenesulphonic chloride in presence of aqueous sodium hydroxide, but with potassium hydroxide yields a small quantity of the *derivative*, $C_{13}H_{19}O_2NS$, melting at 50°. In presence of either sodium or potassium hydroxide, *iso*lupetidine readily yields large quantities of the isomeric compound melting at 65°. The *benzoyl* derivative of lupetidine melts at 111°, that of *iso*lupetidine at 84°. The phenylcarbimide *derivative* of lupetidine melts at 147°, the solubility in benzene at 15° being 0·86 per cent.; the analogous *iso*lupetidine derivative melts at 102°, the solubility being 12·6 per cent. The analogous phenylthiocarbimide *derivatives* of lupetidine and *iso*lupetidine melt at 83—84° and 112—113° respectively.

The benzenesulphonic *derivative* of copellidine is an oil, the analogous *iso*copellidine derivative melts at 66°; the analogous *benzoyl* derivatives are both oils. The phenylcarbimide *derivative* of copellidine melts at 97—98°, and of *iso*copellidine at 232—233°. W. A. D.

Hydrogen Peroxide. By ARTHUR MARCUSE and RICHARD WOLFFENSTEIN (*Ber.*, 1901, **34**, 2430—2432).—Lupetidine combines with concentrated aqueous hydrogen peroxide to form the *salt*, $2C_7H_{15}N,H_2O_2$, which crystallises from ether and melts at 69—70°, the existence of this salt proving the essentially acid nature of hydrogen peroxide. Solutions of the latter, moreover, give an acid reaction, which disappears when the hydrogen peroxide is destroyed by spongy platinum, the solution becoming neutral. W. A. D.

Conversion of Ammonia Derivatives into Ammonium Hydroxides in Aqueous Solutions. By GEORG BREDIG (*Zeit. Elektrochem.*, 1901, **7**, 767—768).—The index of absorption for electrical oscillations of a mixture of equal volumes of pyridine and water is 0·036, that of pyridine alone is 0·018, whilst water alone has a very small absorption. From the conductivity of the mixture an index of absorption 0·005 is calculated.

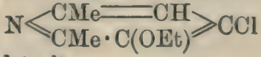
A 66 per cent. solution of betaine has the index of absorption 0·182, the value calculated from its conductivity being 0·0011. Since Drude has shown that a very large index of absorption for electrical oscillations is characteristic of hydroxyl compounds, these results point to the formation of compounds of pyridine and betaine with water.

T. E.

Nitrogenous Bases in Roumanian Petroleum. By Arthur B. Griffiths and N. J. Bluman (*Bull. Soc. Chim.*, 1901, [iii], **25**, 725—726).—The crude petroleum of sp. gr. 0·8445 at 15° was agitated with dilute sulphuric acid and the solution rendered alkaline and extracted with ether; a dark brown, thick, oily liquid boiling at 117° was obtained, which had the composition of pyridine, but differed from this base by being insoluble in water. On reduction, it yielded piperidine, and probably, therefore, was a hydropyridine.

W. A. D.

Action of Phosphorus Oxychloride on Ethyl Aminocrotonate. By August Michaelis and K. von Arend (*Ber.*, 1901, **34**, 2283—2287).—*Chloroethoxylutidine*, $C_9H_{12}ONCl$, prepared by the action of phosphorus oxychloride on ethyl aminocrotonate, is an oil, with a slight odour of pepper, which boils at 132° under 12 mm. pressure, and at 257—260° with slight decomposition under atmospheric pressure, is readily soluble in all organic solvents, but only slightly so in water, has a sp. gr. 1·155 at 17°/17°, n_D 1·5098 at 17°, and a normal molecular weight in freezing benzene. The *hydrochloride*, $C_9H_{12}ONCl,HCl$, is a white, crystalline substance which melts at about 134° and dissolves readily in alcohol or water, but not in ether. The *mercurichloride*, $C_9H_{12}ONCl,HCl,HgCl_2$, forms white crystals and melts at 112—113°. The *platinichloride*, $(C_9H_{12}ONCl)_2,H_2PtCl_6,4H_2O$, forms red crystals, dissolves readily in hot water or alcohol, and melts at 196—198°. The *aurichloride* is an oil which gradually crystallises. The base is converted into lutidine by passing the vapour over heated zinc dust; when boiled with concentrated hydrochloric acid, it loses ethyl chloride and is converted into a crystalline phenolic compound; potassium hydroxide gives a compound $C_9H_{12}O_2NK$, in which the chlorine atom is displaced by the radicle OK. The base is, therefore, regarded as a derivative of 2 : 6-lutidine, and the constitution



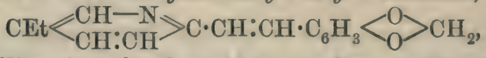
$$N\left\langle\begin{matrix}CMe{=\!=}CH\\CMe\cdot C(OEt)\end{matrix}\right\rangle CCl$$

is provisionally assigned to it.

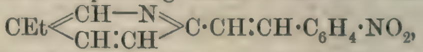
T. M. L.

Action of Aldehydocollidine [2-Methyl-5-ethylpyridine] on Substituted Aromatic Aldehydes. Phenyl-α-picolylalkine [2-β-Hydroxy-β-phenylethylpyridine]. By Hermann Bach (*Ber.*, 1901, **34**, 2223—2237).—2-Methylpyridine reacts with aldehydes in two ways, condensation with elimination of water, and formation of a stilbazole taking place at a high temperature in absence of water, and aldol condensation, with formation of a picolylalkine, occurring at a lower temperature in presence of water. The course of the reaction, however, also depends on the nature of the aldehyde, and the following experiments show that the meta-aldehydes react almost entirely to form stilbazoles, whilst the ortho-aldehydes almost exclusively produce alkines. With the para-aldehydes, the difference is not so marked, but the yield of alkine is much greater than that of stilbazole.

2-Methyl-5-ethylpyridine reacts with piperonal at 230—250° to form a small amount of 3′ : 4′-*methylenedioxy-5-ethyl-2-stilbazole*,



$$CEt{<}\begin{matrix}CH—N\\CH{:}CH\end{matrix}{>}C\cdot CH{:}CH\cdot C_6H_3{<}\begin{matrix}O\\O\end{matrix}{>}CH_2,$$

which crystallises in colourless, silky needles melting at 92°. The *hydrochloride* decomposes at 204°, the *mercurichloride* crystallises in needles melting at 200°, and the *platinichloride* melts and decomposes at 192°. Only a trace of the corresponding alkine could be obtained. 3′-*Nitro-5-ethyl-2-stilbazole*,  $CEt{<}\begin{matrix}CH—N\\CH{:}CH\end{matrix}{>}C\cdot CH{:}CH\cdot C_6H_4\cdot NO_2$, is readily obtained from 2-methyl-5-ethylpyridine, the yield being 85 per cent. of the theoretical; it crystallises in lustrous plates melting at 66°. The *hydrochloride* crystallises in silky needles melting at 194°, the *platinichloride* melts at 178°, and the *aurichloride* at 176°. The *hydrobromide* decomposes at 135°, the *dichromate* melts at 103—104°, and the *picrate* at 220°. No trace of the corresponding alkine could be obtained. Since Castner (this vol., i, 562) and Roth (this vol., i, 165) have shown that *o*-nitrobenzaldehyde gives good yields of alkine, but very small yields of stilbazole, with 2-methyl-5-ethylpyridine and 2-picoline, this points to a marked difference of behaviour between the isomeric aldehydes.

4′-*Nitro-5-ethyl-2-stilbazole*, $C_5NH_3Et\cdot CH{:}CH\cdot C_6H_4\cdot NO_2$, is formed to the extent of about 20 per cent. of the theoretical amount from *p*-nitrobenzaldehyde and 2-methyl-5-ethylpyridine at 160°, and crystallises in lustrous, light yellow plates melting at 116°. The *hydrochloride* crystallises in slender needles, and melts and decomposes at 112°; the *mercurichloride* melts at 188°, the *platinichloride* at 199—200°, and the picrate at 212°. The corresponding p-*nitrophenyl-5-ethyl-2-methylpyridylalkine* [2-*β-hydroxy-β*-p-*nitrophenylethyl-5-ethylpyridine*], $C_5NH_3Et\cdot CH_2\cdot CH(OH)\cdot C_6H_4\cdot NO_2$, is formed to the extent of 70 per cent. from *p*-nitrobenzaldehyde, 2-methyl-5-ethylpyridine, and water at 150°, and crystallises in colourless, silvery plates melting at 147°. The *hydrochloride* melts at 103°, the *mercurichloride* melts and decomposes at 175—180°, the *platinichloride* melts at 141°, and the *picrate* at 126°.

2-*β*-Hydroxy-*β*-phenylethylpyridine, $C_5NH_4\cdot CH_2\cdot CH(OH)Ph$, is converted by reduction into *α*-stilbazoline, which was previously obtained by Baurath (Abstr., 1888, 608) by the reduction of the corresponding *α*-stilbazole; it is also readily converted into the mononitro-derivative, which has been previously prepared synthetically by Roth. The stilbazole, on the other hand, does not give a nitro-derivative (Baurath).

Attempts to resolve 2-*β*-hydroxy-*β*-phenylethylpyridine into its optically active constituents by means of the *d*-tartrate failed, and the base is probably an instance of a partially racemic substance. The *hydrogen* d-*tartrate* crystallises with $2H_2O$ in very slender needles, and melts at 171°. A. H.

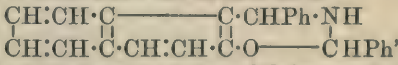
Formation of *ana*-Nitroquinoline [5-Nitroquinoline] from *m*-Nitroaniline. By HERMAN DECKER (*J. pr. Chem.*, 1901, [ii], **63**, 573—576).—By the action of glycerol, sulphuric acid, and nitrobenzene on *m*-nitroaniline, La Coste (Abstr., 1883, 811) prepared phenanthroline, whilst Claus and Stiebel (Abstr., 1888, 295), by the use of picric acid, obtained 10 per cent. of 3-nitroquinoline, together with phenanthroline. By the use of arsenic acid as oxidising agent, the author obtained a mixture of 20 per cent. of 3-nitroquinoline and 80 per cent. of 5-*nitroquinoline*. This compound melts at 72°; the *hydrochloride* forms quadratic plates melting and decomposing at 214°; the *ethiodide*, dark red prisms. On methylation and oxidation, it yields 5-nitromethylquinolone (m. p. 166°). K. J. P. O.

***o*-Toluquinaldine [2:8-Dimethylquinoline]. A Correction.** By ALEXANDER EIBNER (*Ber.*, 1901, **34**, 2450).—The *picrate* of 2:8-dimethylquinoline crystallises from chloroform-alcohol in golden needles or prisms, and melts at 180°, not at 166°, as previously stated (*Ber.*, 1900, **33**, 3467). W. A. D.

Constitution of *p*-Toluquinophthalone [*p*-Methylquinophthalone]. By ALEXANDER EIBNER and E. SIMON (*Ber.*, 1901, **34**, 2303—2311. Compare this vol., i, 348).—*p*-Methylquinophthalone melts at 231—232° (not at 203° as given by Jacobson and Reimer, Abstr., 1884, 335); the *monobromo*-derivative crystallises in six-sided leaflets and melts at 159—160°; the *tribromo*-derivative, obtained by bromination in chloroform solution, crystallises in orange-yellow prisms, melts and decomposes at 233—234°, and in benzene solution decomposes into the crystalline *hydrobromide* of the phthalone; the *mononitro*-derivative crystallises in dark yellow prisms melting at 132°, and the *anil* in small, slender, felted, red needles melting at 233°.

The asymmetric constitution of *p*-methylquinophthalone is proved by the formation of two isomeric methylquinophthalines. p-*Methyl-α-quinophthaline*, $NH{:}C{<}\genfrac{}{}{0pt}{}{C_6H_4}{O}{>}C{:}CH{\cdot}C_9NH_5Me$, obtained by heating the phthalone with alcoholic ammonia at 200°, crystallises in red, felted needles, melts at 270—271°, and when heated with aniline gives the above described anil. p-*Methyl-β-quinophthaline*, obtained by heating *p*-toluquinaldine with phthalimide and zinc chloride, crystallises in lustrous, gold leaflets, and melts at 209°. R. H. P.

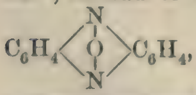
Condensation between β-Naphthol, Aldehydes, and Amines. II. Synthesis of Oxazine Derivatives. By MARIO BETTI (*Gazzetta*, 1901, **31**, i, 377—393. Compare this vol., i, 81).—When the compound $C_{24}H_{19}ON$, obtained by the condensation of β-naphthol, benzaldehyde, and ammonia, and melting at 150° (*loc. cit.*), is boiled with moderately concentrated hydrochloric acid, it undergoes hydrolysis, yielding for each mol. of the compound 1 mol. of benzaldehyde and 1 of *aminobenzylidene-β-naphthol hydrochloride*, $OH{\cdot}C_{10}H_6{\cdot}CHPh{\cdot}NH_2,HCl$. The latter separates from hydrochloric acid in long, lustrous, white needles which begin to redden at 190°, and are not completely melted at 220°; it dissolves in boiling water with slight decomposition, and is very soluble in ethyl or methyl alcohol or acetic acid. In cold aqueous potassium hydroxide it dissolves, imparting a violet fluorescence to the liquid; this solution, when heated, evolves ammonia, whilst when it is kept for a few days, the fluorescence disappears, and is replaced by an orange-yellow colour. The free *aminobenzylidene-β-naphthol*, $C_{17}H_{15}ON$, separates from ether in tufts of long, white needles which melt and decompose at 125°. When boiled with water, in which it is insoluble, or with alcohol or potassium hydroxide solution, which dissolves it, the base decomposes with evolution of ammonia, and, in the case of the last-named solution, of a small quantity of benzaldehyde; it is readily soluble in benzene, acetone, or chloroform, and also in ethyl acetate or acetic acid, undergoing change. With chloroform and potassium hydroxide, it does not give the carbylamine reaction, nor does it yield a colouring matter with furfuraldehyde and acetic acid, as is the case with derivatives containing an amino-group united to the aromatic nucleus. Its *diacetyl* derivative, $C_{21}H_{19}O_3N$, crystallises from dilute alcohol in short, stout prisms melting at 162°. When the base is dissolved in ethyl acetate, intense cooling takes place, and suddenly the liquid is transformed into a voluminous, crystalline paste, which dissolves on further heating with ethyl acetate, the products formed being found to be β-naphthol and the original compound melting at 150°. The latter is also obtained by the condensation of benzaldehyde and aminobenzylidene-β-naphthol in alcoholic solution. From these transformations of the condensation product of β-naphthol, benzaldehyde, and ammonia, the author concludes it must have the constitution

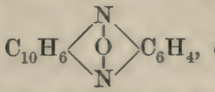


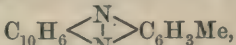
$$\begin{array}{l} CH{:}CH\cdot C\text{————}C\cdot CHPh\cdot NH \\ CH{:}CH\cdot C\cdot CH{:}CH\cdot C\cdot O\text{———}CHPh, \end{array}$$

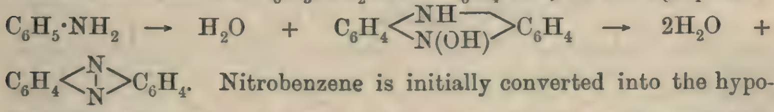
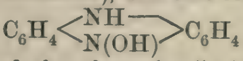
and the name 1 : 3-*diphenyl*-4 : 2-*β-naphtho*iso*oxazine*. Similarly, the compound $C_{30}H_{23}ON$, obtained from β-naphthol, benzaldehyde, and aniline (*loc. cit.*), is 1 : 2 : 3-*triphenyl*-4 : 2-*β-naphtho*iso*oxazine*. It is also obtained by the condensation of benzylideneanil-β-naphthol (see Betti, this vol., i, 81) with benzaldehyde. T. H. P.

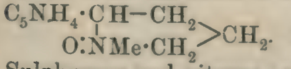
Interaction of Nitrobenzene and Aniline in presence of Alkalis.

By Alfred Wohl and W. Aue (*Ber.*, 1901, **34**, 2442—2450).—When equal weights of aniline and nitrobenzene are heated with four times the quantity of coarsely powdered sodium hydroxide, initially at 140° for 2 hours, finally for a short time at 160°, there is formed 30 per cent. of phenazine, along with about 60 per cent. of the theoretical quantity of azobenzene. When perfectly dry sodium hydroxide is used, and the temperature not allowed to rise above 125°, instead of the phenazine there is formed *phenazine*-5 : 10-*oxide*,  which crystallises from alcohol in slender, yellowish-red needles, melts at 226·5° (corr.), and sublimes in a vacuum at 240—250°; it is a weak base, which is not changed when boiled with acetic anhydride for a short time, although decomposed to form phenazine after boiling for an hour. Reduction with sodium amalgam in alcohol or with zinc dust and hydrochloric acid yields dihydrophenazine; the quantitative reduction of the oxide by stannous chloride requires two more hydrogen atoms than the similar reduction of phenazine.

aβ-Naphthaphenazine-7 : 12-*oxide*,  $C_{10}H_6<\overset{N}{\underset{N}{\overset{|}{\underset{|}{O}}}}>C_6H_4$, obtained along with aβ-naphthaphenazine by the action of dry powdered sodium hydroxide on β-naphthylamine and nitrobenzene at 115—140°, forms green crystals which, when powdered and dried, are yellow; it melts at 182° (corr.), and is easily soluble in all organic solvents. It is shown to contain one oxygen atom more than naphthaphenazine by its quantitative reduction with stannous chloride.

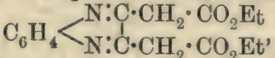
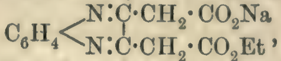
Tolunaphthazine [*methyl-aβ-naphthazine*],  $C_{10}H_6<\overset{N}{\underset{N}{|}}>C_6H_3Me$, prepared by heating β-naphthylamine with *m*-nitrotoluene and dry sodium hydroxide, crystallises from toluene or benzene in yellow needles, melts at 208·5° (corr.), and sublimes under 13 mm. pressure at about 240°.

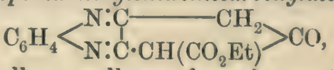
The formation of phenazine from nitrobenzene and aniline in presence of alkali cannot be due to the intermediate production of azo- or azoxy-compounds, since azobenzene and azoxybenzene fail to yield it in presence of alkali, either alone or with aniline or nitrobenzene. *o*-Nitrophenol, moreover, which is formed by the action of alkali hydroxides on nitrobenzene (Abstr., 1900, i, 157), fails to yield phenazine when fused with aniline and an excess of alkali. It is probable that phenazine is formed thus: I. $C_6H_5\cdot NO_2 \rightarrow NO\cdot C_6H_4\cdot OH$; II. $NO\cdot C_6H_4\cdot OH +$  $C_6H_5\cdot NH_2 \rightarrow H_2O + C_6H_4<\begin{matrix}NH—\\ N(OH)\end{matrix}>C_6H_4 \rightarrow 2H_2O + C_6H_4<\overset{N}{\underset{N}{|}}>C_6H_4$. Nitrobenzene is initially converted into the hypothetical *o*-nitrosophenol (from which *o*-nitrophenol would result by a simple oxidation), and this condenses in the manner shown; the compound  $C_6H_4<\begin{matrix}NH—\\ N(OH)\end{matrix}>C_6H_4$ cannot be isolated, but probably is the origin of the phenazine-5 : 10-oxide which is formed from it by the oxidation of two hydrogen atoms. W. A. D.

Action of Hydrogen Peroxide on Tertiary Bases. III. By Martin Auerbach and Richard Wolffenstein (*Ber.*, 1901, 34, 2411—2415. Compare Abstr., 1899, i, 935).—Nicotine oxide (oxynicotine), obtained by Pinner and Wolffenstein (Abstr., 1891, 473, and 1892, 1010) by the action of hydrogen peroxide on nicotine, is shown to be the oxide of a tertiary base, and to have the constitution  $\begin{matrix}C_5NH_4\cdot CH-CH_2\\ \quad | \\ O{:}NMe\cdot CH_2\end{matrix}>CH_2$. The picrate was found to melt at 155—156°. Sulphurous and nitrous acid reduce the oxide to nicotine.

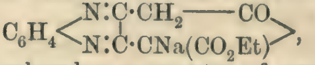
Hydrogen peroxide acts very slowly on *a*- and β-dimethylnaphthylamine. Although small quantities of substance containing oxygen were obtained, oxides of the tertiary bases were not found.

K. J. P. O.

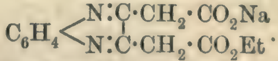
Condensation of Ethyl Cetipate with *o*-Diamines. II. By René Thomas-Mamert and A. Striebel (*Bull. Soc. Chim.*, 1901, [iii], **25**, 712—725. Compare Abstr., 1900, i, 459).—*Ethyl quinoxaline-2 : 3-diacetate*,  $C_6H_4{<}\begin{matrix}N{:}C\cdot CH_2\cdot CO_2Et\\ N{:}C\cdot CH_2\cdot CO_2Et\end{matrix}$, obtained by heating a mixture of ethyl cetipate and *o*-phenylenediamine in alcoholic solution for 1—2 hours at 100°, crystallises from light petroleum in yellow prisms, and melts at 58·2°; with cold dilute aqueous potassium hydroxide (2 mols.), it yields, after several days, a solution which, on adding dilute sulphuric acid, gives a yellow precipitate of indefinite composition. This dissolves in warm sodium carbonate, and the solution on cooling yields the *sodium* salt,  $C_6H_4{<}\begin{matrix}N{:}C\cdot CH_2\cdot CO_2Na\\ N{:}C\cdot CH_2\cdot CO_2Et\end{matrix}$, in golden-yellow needles; on adding dilute sulphuric acid to the solution of the sodium salt, *ethyl benzo-β-ketopentamethyleneazinecarboxylate*,

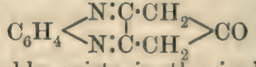
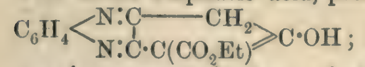
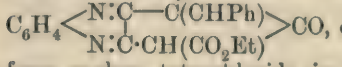

$$C_6H_4{<}\begin{matrix}N{:}C\text{———}CH_2\\ N{:}C\cdot CH(CO_2Et)\end{matrix}{>}CO,$$

separates in golden-yellow needles, and can be crystallised from chloroform; it decomposes without melting. Ethyl quinoxalinediacetate is not acted on by sodium ethoxide in absolute ethereal solution, but in alcoholic solution yields the *sodium* derivative,

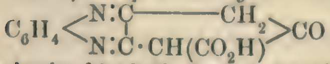
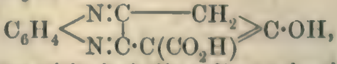

$$C_6H_4{<}\begin{matrix}N{:}C\cdot CH_2\text{——}CO\\ N{:}C\cdot CNa(CO_2Et)\end{matrix}{>},$$

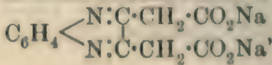
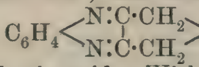
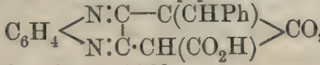
which crystallises in spherular aggregates of greenish-yellow needles, and is decomposed by water to form the sodium salt,

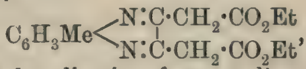

$$C_6H_4{<}\begin{matrix}N{:}C\cdot CH_2\cdot CO_2Na\\ N{:}C\cdot CH_2\cdot CO_2Et\end{matrix}.$$

The latter is also readily formed on warming ethyl benzo-β-ketopentamethyleneazinecarboxylate with aqueous sodium carbonate. Ethyl benzo-β-ketopentamethyleneazinecarboxylate, since it fails to yield either an oxime or a hydrazone, and does not lose carbon dioxide and alcohol to form the compound  $C_6H_4{<}\begin{matrix}N{:}C\cdot CH_2\\ N{:}C\cdot CH_2\end{matrix}{>}CO$ when heated with dilute sulphuric acid, probably exists in the isodynamic form,  $C_6H_4{<}\begin{matrix}N{:}C\text{——}CH_2\\ N{:}C\cdot C(CO_2Et)\end{matrix}{\geqslant}C\cdot OH$; it does not interact with benzaldehyde save in presence of a trace of piperidine (compare Schiff, Abstr., 1898, i, 237 and 355), when it readily yields the *benzylidene* derivative,  $C_6H_4{<}\begin{matrix}N{:}C\text{—}C(CHPh)\\ N{:}C\cdot CH(CO_2Et)\end{matrix}{>}CO$, of the ketonic form, which crystallises from carbon tetrachloride in yellowish-orange leaflets, and melts at 203°. It should be noted, however, that it does not yield an acetyl derivative with acetic anhydride.

Benzo-β-ketopentamethyleneazinecarboxylic acid,

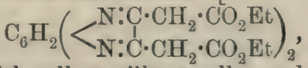

$$C_6H_4{<}\begin{matrix}N{:}C\text{———}CH_2\\ N{:}C\cdot CH(CO_2H)\end{matrix}{>}CO$$
or

$$C_6H_4{<}\begin{matrix}N{:}C\text{——}CH_2\\ N{:}C\cdot C(CO_2H)\end{matrix}{\geqslant}C\cdot OH,$$

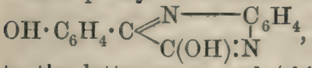
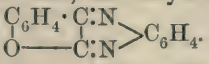
is obtained by hydrolysing the ethyl ester with alcoholic sodium ethoxide (2 mols.), and decomposing the *sodium* salt,  $C_6H_4{<}\begin{matrix}N{:}C\cdot CH_2\cdot CO_2Na\\ N{:}C\cdot CH_2\cdot CO_2Na\end{matrix}$, which could not be isolated, with dilute sulphuric acid; it crystallises from alcohol in silky, golden-yellow needles, decomposes without melting at about 200°, and does not lose carbon dioxide to form the compound  $C_6H_4{<}\begin{matrix}N{:}C\cdot CH_2\\ \mid \\ N{:}C\cdot CH_2\end{matrix}{>}CO$, when heated for several hours with dilute sulphuric acid. With benzaldehyde in boiling carbon tetrachloride solution in presence of a trace of piperidine, it readily yields the *benzylidene* derivative,  $C_6H_4{<}\begin{matrix}N{:}C\text{—}C(CHPh)\\ \mid \\ N{:}C\cdot CH(CO_2H)\end{matrix}{>}CO$, which crystallises in yellow needles and melts at 198°.

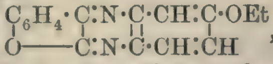
Ethyl 6-methylquinoxaline-2:3-diacetate,  $C_6H_3Me{<}\begin{matrix}N{:}C\cdot CH_2\cdot CO_2Et\\ \mid \\ N{:}C\cdot CH_2\cdot CO_2Et\end{matrix}$, obtained from ethyl cetipate and 3:4-tolylenediamine, forms yellow prisms and melts at 59°.

Ethyl methylbenzo-3-ketopentamethyleneazinecarboxylate decomposes without melting at 200°; its *benzylidene* derivative forms orange-coloured needles and melts at 198°.

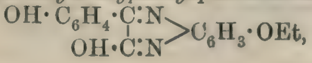
Methylbenzo-β-ketopentamethyleneazinecarboxylic acid crystallises in yellow needles and decomposes at about 220°; its *benzylidene* derivative melts above 200°.

With 1:2:3:4-tetraminobenzene, ethyl cetipate condenses to form *ethyl 1:2:3:4-diquinoxalinetetracetate* [1:4:7:10-*naphthatetrazine-2:3:8:9-tetracetate*],  $C_6H_2\left({<}\begin{matrix}N{:}C\cdot CH_2\cdot CO_2Et\\ \mid \\ N{:}C\cdot CH_2\cdot CO_2Et\end{matrix}\right)_2$, which crystallises from alcohol in brownish-yellow, silky needles and melts at 128°; the analogous compound from 1:2:4:5-tetraminobenzene forms orange leaflets and melts at 143°, that from 2:3:4:5-tetraminotoluene forming silky, yellow needles and melting at 153°. Alcoholic sodium ethoxide converts the last of these into the *compound* $C_{23}H_{20}O_6N_4$, which is a yellow powder decomposing at 220°. W. A. D.

Isatin and its Derivatives. By LEO MARCHLEWSKI and J. SOSNOWSKI (*Ber.*, 1901, **34**, 2294—2298).—By the action of nitrous acid, isatic acid is converted into o-*hydroxybenzoylformic acid*, $OH\cdot C_6H_4\cdot CO\cdot CO_2H$, which forms a yellow *sodium* salt, and condenses with *o*-phenylenediamine to 2-hydroxy-3-*o*-hydroxyphenylquinoxaline,  $OH\cdot C_6H_4\cdot C{\ll}\begin{matrix}N\text{——}C_6H_4\\ \quad\quad\mid \\ C(OH){:}N\end{matrix}$, thus confirming the constitution assigned to the latter compound (this vol., i, 415). By distilling the barium salt of the sulphonic acid, the dihydroxy-compound is converted into coumarophenazine,  $\begin{matrix}C_6H_4\cdot C{:}N\\ \mid \quad\quad \mid \\ O\text{——}C{:}N\end{matrix}{>}C_6H_4$.

Ethoxycoumarophenazine,  $\begin{matrix}C_6H_4\cdot C{:}N\cdot C\cdot CH{:}C\cdot OEt\\ \mid \quad\quad \mid \quad\; \| \quad\quad \mid \\ O\text{——}C{:}N\cdot C\cdot CH{:}CH\end{matrix}$, prepared by the action of nitrous acid on the condensation product of acetylisatin with ethoxy-*o*-phenylenediamine, crystallises in minute, white needles and melts at 162·5°.

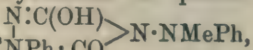
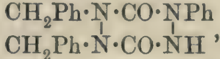
2-Hydroxy-7-ethoxy-3-o-hydroxyphenylquinoxaline,



$$\begin{matrix}OH\cdot C_6H_4\cdot C{:}N\\ \mid \\ OH\cdot C{:}N\end{matrix}{>}C_6H_3\cdot OEt,$$

prepared by the action of ethoxy-*o*-phenylenediamine on hydroxybenzoylformic acid, crystallises in yellow needles and melts at 242—243°.

T. M. L.

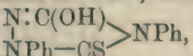
Constitution of Urazines. By MAX BUSCH (*Ber.*, 1901, **34**, 2311—2320. See this vol., i, 488).—The following new compounds, obtained by methods previously described (*loc. cit*), were prepared:—*ethyl* 2-*phenyl*-5-*methylphenylcarbazide*-1-*carboxylate*, which crystallises in small, colourless needles and melts at 164—165°; *ethyl* 2-*phenyl*-4-*methylphenylsemicarbazidecarboxylate*, which crystallises in prisms melting at 117°; 1-*phenyl*-4-*methylanilinourazole*,  $\left.\begin{array}{l}N{:}C(OH)\\ |\\ NPh\cdot CO\end{array}\right>N\cdot NMePh$, which crystallises in lustrous, colourless leaflets, melts at 167—168°, forms a *methyl* ether which crystallises in clusters of small needles softening at 101° and melting at 103°, and, when treated with hydriodic acid, forms 1-phenyl-4-anilinourazole; *ethyl* 2-*phenyl*-4:5-*dibenzylcarbazide*-1-*carboxylate*, which crystallises in four-sided tablets, melts at 105°, and, when treated with alcoholic potash, yields *phenyldibenzylurazine*,  $\begin{array}{l}CH_2Ph\cdot N\cdot CO\cdot NPh\\ \quad\quad\quad\;\; |\quad\quad\quad\; |\\ CH_2Ph\cdot N\cdot CO\cdot NH\end{array}$, which crystallises in colourless leaflets, melts at 180°, has a neutral reaction, and is the first known urazine (see Busch, *loc. cit.*).

R. H. P.

Syntheses in the Urazole Series. By MAX BUSCH and ALFRED GROHMANN (*Ber.*, 1901, **34**, 2320—2331).—Urazoles and thiourazoles (from the thiocarbazides $NR'_2\cdot NH\cdot CS\cdot NR\cdot NH\cdot CO_2Et$) have been prepared by methods previously described (this vol., i, 488). *Ethyl* 2-*phenyl*-5-p-*anisylcarbazide*-1-*carboxylate* crystallises in small, colourless needles and melts at 161—162°. *Ethyl* 2-p-*anisyl*-5-*phenylcarbazide*-1-*carboxylate* crystallises in aggregates of small, slender needles and melts at 184°. *Ethyl* α-*naphthylcarbazinate* crystallises in leaflets and melts at 107—108°, and the *chloride*, $C_{10}H_7\cdot N(COCl)\cdot NH\cdot CO_2Et$, melts about 115°; 1-α-*naphthyl*-4-*aminourazole* crystallises in compact tablets, which soften at 196° and melt at 201°. *Ethyl* β-*naphthylcarbazinate* crystallises in needles and melts at 105·5°; the analogous chloride crystallises in silky needles and melts at 139°, and 1-β-*naphthyl*-4-*aminourazole* crystallises in lustrous, white leaflets melting at 265°. The naphthylaminourazoles, when treated with nitrous acid, yield the naphthylurazoles, α-*naphthylurazole* crystallises in clusters of lustrous, small needles melting at 233—234°, and β-*naphthylurazole* in mossy needles melting at 287°.

Ethyl 2:4-*diphenylthiosemicarbazide*-1-*carboxylate*,

$$NHPh\cdot CS\cdot NPh\cdot NH\cdot CO_2Et,$$

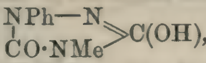
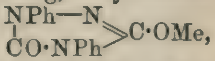
crystallises in slender needles, melts at 145°, and, when hydrolysed, yields 1:4-*diphenyl*-5-*thiourazole*,  $\left.\begin{array}{l}N{:}C(OH)\\ |\\ NPh{-}CS\end{array}\right>NPh$, which crystallises in small, slender needles melting at 214—215°. 4-*Amino*-5-*thio*-1-*phenylurazole* crystallises in felted needles, melts and decomposes at 191—192°, and, when treated with nitrous acid, yields 5-*thio*-1-*phenylurazole*, which crystallises in laminæ melting at 229—230°, and a microcrystalline powder melting at 220°, which is probably a *disulphide*. *Ethyl* 2:5-*phenylthiocarbazide*-1-*carboxylate* crystallises in white leaflets melting at 138°, and 5-*thio*-1-*phenyl*-4-*anilinourazole* melts at 184°. *Ethyl*-2-*phenyl*-5-p-*tolylthiocarbazide*-1-*carboxylate* crystallises in clusters of small needles melting at 133°, and 5-*thio*-4-p-*toluidino*-1-*phenylurazole* in slender needles melting at 190°. *Ethyl* p-*tolylhydrazine*-*a*-*thiocarbonylchloride*-*β*-*carboxylate* was obtained in the form of yellowish needles melting at 109—110°, *ethyl* 5-*phenyl*-2-p-*tolylthiocarbazide*-1-*carboxylate* as compact crystals melting at 125°, and 5-*thio*-4-*anilino*-1-p-*tolylurazole* as slender needles melting at 219°.

R. H. P.

1 : 4-Dialkylurazoles. By MAX BUSCH and C. HEINRICHS (*Ber.*, 1901, **34**, 2331—2339).—The α-carbonyl chlorides of carbazinates react with primary amines, forming 2 : 4-dialkylsemicarbazide-1-carboxylates, which, when hydrolysed, yield 1 : 4-dialkylurazoles.

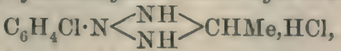
Ethyl 2-phenyl-4-methylsemicarbazide-1-carboxylate,

$$NHMe\cdot CO\cdot NPh\cdot NH\cdot CO_2Et,$$

crystallises in colourless needles and melts at 131° ; 1-*phenyl*-4-*methylurazole*,  $\begin{array}{l}\text{NPh—N}\\ \text{CO·NMe}\end{array}\!\!>\text{C(OH)}$, crystallises in lustrous, colourless needles, melts at 224°, forms a *sodium* salt which crystallises in lustrous, small, felted needles, and, when treated with acetic anhydride and sodium acetate, an *acetyl* derivative which crystallises in colourless needles and melts at 129°. *Ethyl* 2-*phenyl*-4-*methylsemicarbazide*-1-*carboxylate* crystallises in nodules of small, colourless needles melting at 113° ; 1-*phenyl*-4-*methylurazole* crystallises in lustrous laminæ and melts at 174°. *Ethyl* 2-*phenyl*-4-*benzylsemicarbazide*-1-*carboxylate* crystallises in clusters of needles melting at 143—144°, and 1-*phenyl*-4-*benzylurazole* in tablets melting at 232°. *Ethyl* 2 : 4-*diphenylsemicarbazide*-1-*carboxylate* crystallises (with $\frac{1}{2}$EtOH) in prisms melting at 123° (without the alcohol of crystallisation at 131°) ; 2 : 4-*diphenylurazole* crystallises in lustrous leaflets, melts at 163°, and forms *potassium* (small, felted needles), *sodium* (lustrous needles), and *calcium* salts (microscopic leaflets), an *acetyl* derivative, which crystallises in long, silky needles melting at 166°, and a *methyl* ether (probably),  $\begin{array}{l}\text{NPh—N}\\ \text{CO·NPh}\end{array}\!\!>\text{C·OMe}$, which crystallises in long, brittle needles melting at 134°. *Ethyl* 2-*phenyl*-4-p-*tolylsemicarbazide*-1-*carboxylate* crystallises in leaflets melting at 134°, and 1-*phenyl*-4-p-*tolylurazole* in small, slender, felted needles melting at 189—190°. *Ethyl* p-*tolylcarbazinate* crystallises in pale yellow, compact needles melting at 89—90°, the *chloride* of the α-carboxylate in small, white needles melting at 94°, *ethyl* 4-*phenyl*-2-p-*tolylsemicarbazide*-1-*carboxylate* in very lustrous, flat needles melting at 96—97°, and 4-*phenyl*-1-p-*tolylurazole* in lustrous laminæ which soften at 195° and melt at 201°.

R. H. P.

Triazan Derivatives. III. By HUGO VOSWINCKEL (*Ber.*, 1901, **34**, 2349—2354. Compare Abstr., 1899, i, 958, and this vol., i, 53).—p-*Chlorophenylmethyl*cyclo*methylenetriazan hydrochloride*,



$$C_6H_4Cl\cdot N{<}\begin{array}{c}NH\\ NH\end{array}{>}CHMe,HCl,$$

is prepared by reducing chlorophenylmethoxy*cyclo*methylenetriazan with stannous chloride in alcoholic solution (*loc. cit.*) ; from hydrochloric acid, the salt crystallises in colourless leaflets, from alcohol and ether in prisms containing alcohol which melt at 100°; the dry salt melts at 197°. The free *base* is an oil which readily decomposes.

On reducing chlorophenylmethoxy*cyclo*methylenetriazan with a boiling aqueous solution of ammonium sulphide, *p*-chlorophenylhydrazine (m. p. 88°) is formed.

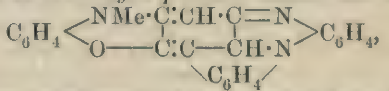
All attempts to prepare derivatives of phenyltriazan by reduction of phenylnitrosohydrazine or its acyl derivatives failed.

Benzoylphenylnitrosohydrazine, $NO\cdot NPh\cdot NHBz$, prepared by the action of nitrous acid on benzoylphenylhydrazine in alcoholic suspension, crystallises in yellow needles melting and decomposing at 110°. This substance gives Liebermann's reaction, dissolves in sulphuric acid forming a carmine solution, and also in aqueous alkalis and ammonia.

Potassium phenylnitrosohydrazine sulphonate, $NO\cdot NPh\cdot NH\cdot SO_3K$, prepared by the action of nitrous acid on potassium phenylhydrazinesulphonate, forms yellowish-white needles which decompose at 250°, dissolve readily in alkalis, and give Liebermann's reaction.

K. J. P. O.

Base from N-Methyltriphenoxazinephenazonium Salts (N-Methyltriphenazinoxazinecarbazole). By EMIL DIEPOLDER (*Ber.*, 1901, 34, 2272—2276).—N-*Methyltriphenoxazinephenazonium nitrate*, $C_{25}H_{18}O_4N_4,2H_2O$, crystallises in golden needles; it is prepared in manner similar to the chloride (Abstr., 1900, i, 192), but a better yield is obtained. The chloride is reduced to a leuco-compound by stannous chloride, or by zinc dust and acetic acid. Sodium hydroxide precipitates from a solution of the nitrate an *anhydro-base*, $C_{25}H_{17}ON_3$, which is regarded as N-*methyltriphenazinoxazinecarbazole*,

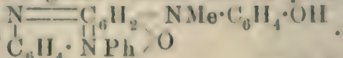


$$C_6H_4\left<\begin{array}{l}NMe\cdot C{:}CH\cdot C{=}N\\ O{-}{-}C{:}C{-}{-}CH\cdot N\\ \qquad\quad \diagdown C_6H_4 \diagup\end{array}\right>C_6H_4,$$

the hydroxyl group being assumed to wander from the nitrogen atom to a carbon atom, and then to be eliminated with a hydrogen atom to form a new five-membered ring; the base contains seven rings and is exceedingly stable; it does not melt at 330°, is not attacked by sodium acetate and acetic anhydride, and is not decomposed by heating at 200° with dilute sulphuric acid; it is obtained in needles with a bronze-like lustre when sublimed, or when crystallised from ethyl benzoate, but crystallises from nitrobenzene or benzene with a green lustre; it dissolves in 25 parts of boiling nitrobenzene, 30 parts of boiling ethyl benzoate, 200 parts of boiling chloroform, and 600 parts of boiling benzene. The *hydrochloride*, $C_{25}H_{17}ON_3,HCl,2H_2O$, forms needles having a greenish lustre; the *platinichloride*,

$$(C_{25}H_{17}ON_3)_2,H_2PtCl_6,$$

is a flocculent, blue precipitate. When decomposed by alkalis, the anhydro-base gives methyl-*o*-aminophenol, hydroxyaposafranone, and a substance which melts at 240°, crystallises from a mixture of benzene and alcohol in brown needles with a green lustre, and is perhaps *o*-hydroxymethylanilinoaposafranone,



$$\begin{array}{l}N{=}{=}C_6H_2{<}NMe\cdot C_6H_4\cdot OH\\ C_6H_4\cdot NPh{>}O\end{array}.$$

T. M. L.

Azo-derivatives of *o*-Nitro-*p*-toluidine. By KARL ELBS and B. SCHWARZ (*J. pr. Chem.*, 1901, [ii], 562—568).—The mixture of *p*-diamino-*o*-azoxytoluene and *p*-diamino-*o*-azotoluene, obtained in the electrolytic reduction of *o*-nitro-*p*-toluidine (Abstr., 1899, i, 270), forms mixed crystals melting at 132—133°; the two substances can only be separated by recrystallisation of their hydrochlorides. The pure azo-derivative can be obtained free from the azoxy-compound by converting the latter into diaminohydroxyazotoluene by means of sulphuric acid.

p-*Diamino*-o-*azoxytoluene*, $N_2O(C_6H_3Me{\cdot}NH_2)_2$, crystallises in golden-yellow, silky needles melting at 148—148·5°; the *dihydrochloride* forms pale yellow, lustrous leaflets, which decompose on heating without melting; the *platinichloride*, pale yellow, microscopic needles; the *sulphate*, yellowish needles. The *diacetyl* derivative, $C_{14}H_{14}ON_4(OAc)_2$, forms dirty yellow crystals, melting and decomposing at 280—281°.

p-*Diamino*-o-*azotoluene*, $N_2(C_6H_2Me{\cdot}NH_2)_2$, prepared most easily by the oxidation of the corresponding hydrazo-derivative by sodium hydroxide and air, forms dark red needles or bronze-coloured leaflets melting at 158—159°. The *hydrochloride* crystallises in thin, pale brown leaflets, which decompose without melting, and are less soluble in dilute hydrochloric acid than the hydrochloride of the azoxy-derivative; the *platinichloride* forms a pale brown powder; the *sulphate*, microscopic, pale brown needles.

p-*Diamino*-m-*hydroxy*-o-*azotoluene*,

$$NH_2{\cdot}C_6H_3Me{\cdot}N_2{\cdot}C_6H_2Me(OH){\cdot}NH_2,$$

is prepared by the action of concentrated sulphuric acid at 100° on *p*-diamino-*o*-azoxytoluene; on pouring the product into water, the sulphate separates. The hydroxyazo-compound crystallises in deep red needles melting and decomposing at 176—178°; the *sulphate* forms dark reddish-brown leaves.

p-Diamino-*o*-hydrazotoluene, $N_2H_4(NH_2{\cdot}C_6H_3Me)_2$, is best prepared by the electrolytic reduction either of the azo- or the azoxy-compound, or of a mixture of the two dissolved in dilute alcohol, in the presence of sodium acetate; the yield is 80 per cent. of the calculated quantity (compare *loc. cit.*). K. J. P. O.

Sensitiveness of Diazo-compounds, especially of 3-Diazocarbazole, to Light. Some new Derivatives of Carbazole. By OTTO RUFF and VICTOR STEIN (*Ber.*, 1901, 34, 1668—1684).—The following methods give beautiful, brown photographic prints, with clear, permanent tones; the first method is used for positives and the second for negatives.

I. A gelatin photographic paper, hardened with formaldehyde, is saturated on the prepared side with a 2 per cent. solution of diazocarbazole zincochloride, dried, and exposed to light passing through the positive; the print is developed and fixed by a 1 per cent. alkaline solution of α-naphthol, which produces an orange-yellow picture which is toned to brown by a bath of dilute acetic acid. The light passing through the clear parts of the positive destroys the diazo-salt and renders it unable to combine with the naphthol to form a dye. Using

β-naphthol, phloroglucinol, resorcinol, or *m*-tolylenediamine instead of α-naphthol, dark red, violet, yellowish-brown, or brownish-violet prints are respectively obtained.

II. The paper is soaked in a solution containing sodium carbazolediazosulphonate and a naphthol or an amine, dried, and exposed under the negative; where light passes through, the formation of a dye occurs, and the print is fixed by washing with hot water, dilute sodium hydroxide, cold water, dilute acetic acid, and finally water. The following colours are produced by certain naphthols; α-naphthol brown, β-naphthol red, 2-naphthol-6- and -4-sulphonic acids violet, the 3 : 6-disulphonic acid bluish-violet, and *m*-tolylenediamine brown.

The prints are permanent, and the original unexposed paper can be kept for long periods without ill effects.

The following facts are established with regard to the action of light on substituted diazobenzene chlorides. Those which contain a negative group (OH,NO_2,CO_2H) in the para-position are more sensitive than those containing a similarly situated positive group (Cl,CH_3); the influence of the nitro-group is greatest. Ortho- and para-substituted groups have about the same effect, either in increasing or decreasing sensitiveness; this effect is always less than the effect of a meta-group. In the case of diazo-salts derived from different nuclei, the sensitiveness to light increases with the "number of atoms in the nucleus"; thus the diazo-salt from 3-aminocarbazole is nearly five times as sensitive as that from *p*-toluidine. As regards the decomposition of diazo- and tetrazo-compounds, an equal number of diazo-groups are destroyed by light in the same time; thus the same number of minutes is necessary to decompose completely the diazo-salt from an *N*/40 solution of *p*-aminodiphenyl as from an *N*/20 solution of benzidine.

Nitroso-3-nitrocarbazole, obtained by passing gaseous nitrous acid, evolved from starch and nitric acid, into carbazole dissolved in glacial acetic acid, crystallises from alcohol in bright yellow needles, melts at 166·5° (corr.), and on boiling with amyl alcohol yields 3-nitrocarbazole (m. p. 208·5° corr.; Mazzara, Abstr., 1891, 570, and Votočka, *Rozpravy ceské Akad.*, 5, ii, No. 22, give 209° and 210° respectively). When reduced with stannous chloride, it gives 3-aminocarbazole, which darkens at 240° and melts and decomposes at 259° (corr., Mazzara gives 246—248°, Votočka 248° and 256°). 3-Diazocarbazole chloride yields well-defined salts with zinc chloride and mercuric chloride; the dyes derived from it are of small tinctorial value. *Sodium carbazolediazosulphonate* apparently exists in two modifications; the *labile* form is orange-yellow and changes to the *stable* form on heating with water, from which the latter crystallises in needles. When reduced with sodium amalgam, *sodium carbazole*-3-*hydrazinosulphonate* is obtained in yellowish, ill-defined crystals. 3-*Hydroxycarbazole* is only formed in small quantity (10 per cent.) on boiling 3-diazocarbazole with water; it crystallises from xylene in small, feebly yellow needles, melts at 260—261° (corr.), and yields a *diacetyl* derivative, crystallising in colourless needles and melting at 113—114°.

When 3-aminocarbazole is heated with acetic anhydride for 8 hours at 180°, a mixture of the *diacetyl* and *triacetyl* derivatives is obtained;

the former crystallises from absolute alcohol in microscopic needles and melts at 199·5° (corr.), whilst the latter forms larger needles and melts at 174·5° (corr.). On nitration at 60°, the triacetyl derivative yields *nitrodiacetyl-3-aminocarbazole*, which crystallises from alcohol in small, yellow needles and melts at 199·5° (corr.).

W. A. D.

Action of Alkylmalonic Esters on Diazonium Chlorides. By G. Favrel (*Compt. rend.*, 1901, **132**, 1336—1338).—The alkylmalonic esters react with diazonium chlorides in accordance with the following equation, $Ph{\cdot}N{:}N{\cdot}OH + CHR(CO_2Et)_2 = Ph{\cdot}NH{\cdot}N{:}CR{\cdot}CO_2Et + CO_2 + Et{\cdot}OH$, yielding substituted hydrazones of the pyruvic acid series. The reaction has been generalised by employing the ethyl esters of both methyl- and ethyl-malonic acids and the diazonium salts derived from aniline and the toluidines. G. T. M.

Synthesis of *o*-Azidobenzaldehyde [*o*-Triazobenzaldehyde]. By Eugen Bamberger and Ed. Demuth (*Ber.*, 1901, **34**, 2292—2293). —*o*-Triazobenzaldehyde, $CHO{\cdot}C_6H_4{\cdot}N_3$, can be synthesised by the action of azoimide on *o*-diazobenzaldehyde, and is identical with the substance prepared indirectly from indiazonoxime (this vol., i, 392).

T. M. L.

Combination of Sodium Tetrazoditolyldisulphonate with β-Naphthylethylamine. Production of a Colouring Matter. By Alphonse Seyewetz and Blanc (*Compt. rend.*, 1901, **133**, 38—41). —The action of β-naphthylethylamine hydrochloride on sodium tetrazoditolyldisulphonate in presence of water yields a yellow oil which gradually becomes crystalline, and can be recrystallised from dilute alcohol (3 : 10) at a temperature not exceeding 80°. It has the composition $C_{12}H_6Me_2[NH{\cdot}N(SO_3H){\cdot}C_{10}H_6{\cdot}NHEt]_2$, decomposes at about 160° without melting, and is insoluble in ether, benzene, or chloroform. When exposed to light, it is converted into a red colouring matter, $C_{12}H_6Me_2(N_2{\cdot}C_{10}H_6{\cdot}NHEt)_2$, which decomposes at 150° without melting, is somewhat soluble in alcohol, very slightly so in ether, and insoluble in dilute acids, but dissolves readily in acetone or acetic acid. It is identical with the colouring matter obtained by the action of naphthylethylamine hydrochloride on tetrazotolidine.

C. H. B.

Precipitability of Proteids by Chloroform. By Friedrich Krüger (*Zeit. Biol.*, 1901, **41**, 341—359).—The paper is largely occupied with a discussion of the results of others relating to the applicability of chloroform as a means of precipitating and separating proteids. Special attention was given to a proteid named *mucosalbumin*, which was precipitated by chloroform from extracts of mucous membranes of the stomach and intestine. Analyses do not give concordant results. W. D. H.

Compounds of certain Proteids with Hydrogen Chloride. By Walter Erb (*Zeit. Biol.*, 1901, **41**, 309—330).—Proteids behave toward hydrogen chloride as bases, and form salts with it. These proteid salts show hydrolytic dissociation to a great extent, and thus the various contradictory statements regarding the acid compounds of proteids are explained.

Hetero-albumose, phyto-vitellin, egg-albumin, and serum-albumin were the proteids experimented with, and were prepared in a pure condition. They show different maximal acid capacities, and dissociation curves of different slopes. These properties are regarded as characteristic of the individual proteids. W. D. H.

Glucoproteins as new chemically definite Culture Media for the Study of Micro-organisms. By CHARLES LEPIERRE (*Compt. rend.*, 1901, **133**, 113—116).—In the glucoproteins, the author finds a simple material of definite chemical character, from which a great number of micro-organisms (pathogenic and otherwise) are able to obtain their nitrogen. By the hydrolysis of proteids or gelatin at 100° by barium hydroxide (a modification of Schützenberger's method, Abstr., 1886, 270), a series of glucoproteins have been prepared in a pure and crystalline state. They have the general formula $C_nH_{2n}O_4N_2$ (where $n = 6—11$); from gelatin, the members of the series with six and seven carbon atoms have been obtained; from albumin or fibrin, the members with 8, 9, 10, and 11 carbon atoms. The constitution of the substance with seven carbon atoms is thus represented:

$$CO_2H{\cdot}CH_2{\cdot}NH{\cdot}[CH_2]_2{\cdot}NH{\cdot}CHMe{\cdot}CO_2H.$$

The culture-media consist of water (100 grams), glucoprotein (1·5—2 grams), glycerol, dextrose, or sucrose (2—3 grams), sodium chloride and magnesium sulphate (each 0·5 gram), calcium glycerophosphate (0·2—0·3 gram), and potassium hydrogen carbonate (0·1—0·2 gram).

The author has observed that certain bacteria prefer certain glucoproteins. K. J. P. O.

Action of Nascent Chlorine on Casein. By JOSEF HABERMANN and R. EHRENFELD (*Zeit. physiol. Chem.*, 1901, **32**, 467—475).—Casein is dissolved in 5 per cent. potassium hydroxide mixed with finely divided potassium chlorate, and treated for some 48 hours at the ordinary temperature with hydrogen chloride. A flocculent precipitate is produced on the addition of water, and this, although free from phosphorus and containing some 13—14 per cent. of chlorine yields, on treatment with hydrochloric acid and stannous chloride, with bromine water or on fusion with potassium hydroxide, products practically identical with those obtained from casein itself under similar treatment. J. J. S.

Formation of Leucinimide by the Peptic and Trypsic Fermentation of Oxyhæmoglobin and of Globin. By SERGEI SALASKIN (*Zeit. physiol. Chem.*, 1901, **32**, 592—597).—A leucinimide melting at 295—296°, and apparently identical with the substance described by Cohn (Abstr., 1896, i, 658), has been obtained by the trypsic fermentation of oxyhæmoglobin. A similar compound is also formed by the peptic fermentation of this substance, but no product of definite melting point was obtained, fusion occurring at temperatures ranging from 250° to 273—274°. J. J. S.

Proteinochrome. By FERD. KLUG (*Pflüger's Archiv*, 1901, 86, 194—198).—Pancreatic tissue was allowed to digest itself, and the product shaken with alcohol and ether and centrifugalised; the substance, *proteinochrome*, which gives the characteristic violet-red coloration with chlorine water is present in the lowest strata. By repeated centrifugalising with ether, it is claimed that the substance was obtained in a pure condition, and to it the formula $C_4H_8O_2N$ is assigned. W. D. H.

Preparation and Analysis of some Nucleic Acids. By P. A. LEVENE (*Zeit. physiol. Chem.*, 1901, 32, 541—551).—In addition to the analyses previously given (this vol., i, 299), numbers are now given for acids obtained from spleen and from yeast.

Nucleic acid from	C.	H.	N.	P.
Spleen	36·40	5·24	17·30	9·03
Yeast	36·65	4·57	17·89	8·93

J. J. S.

Albumin Peptones. By CARL PAAL (*Chem. Centr.*, 1901, i, 1338—1339; from *Festschr. Univ. Erlangen zur Feier S. K. H. des Prinzregenten Luitpold*. Compare Abstr., 1898, i, 456).—Albumin peptones have been isolated from the mixture of hydrochlorides of albumoses and peptones obtained by digesting egg-albumin with dilute hydrochloric acid. In one case, the albumoses were removed by saturating the aqueous solution with ammonium sulphate. The concentrated solution of the free peptones prepared from the hydrochlorides, when poured into absolute alcohol, gave a precipitate which contained C 44·50 and N 14·87, whilst the filtrate yielded a residue containing C 47·77 and N 12·55 per cent. In a second experiment, the albumoses were removed by saturating the aqueous solution with zinc sulphate, and treating the filtrate with phosphotungstic acid. The solution of the peptones obtained from the precipitate in this case gave a precipitate with alcohol which contained C 50·10 and N 15·58, the residue from the filtrate containing C 52·63 and N 13·76 per cent. The filtrate from the phosphotungstic acid precipitate after removing the acids yielded a peptone insoluble in alcohol and containing C 40·71 and N 9·6, and a soluble peptone containing C 44·28 and N 11·37 per cent. Both these substances give only a faint biuret reaction, and are to be regarded as intermediate products, being related, on the one hand, to the real peptones which are precipitated by phosphotungstic acid, and on the other hand to the amino-acids. The peptones obtained in the first case by means of ammonium sulphate must therefore consist of a mixture of real peptones with intermediate products. E. W. W.

Intracellular Diastases of the Amœba. By H. MOUTON (*Compt. rend.*, 1901, 133, 244—246).—A species of amœba existing abundantly in garden soil was found to contain a diastase capable of liquefying gelatin and digesting dead microbes in presence of chloroform. It also acts distinctly on albumin coagulated by heat, but seems to be without action on fibrin previously heated to 58°. The activity of the diastase is shown only in feebly alkaline media and is destroyed at a temperature of 60°. C. H. B.

Production of Casease by a Parasitic Streptothrix. By E. Bodin and C. Lenormand (*Ann. Inst. Pasteur*, 1901, **15**, 279—288).—The parasitic *Streptothrix*, *Oospora* of the *Microsporum*, found in the horse (*Arch. de parasit.*, 1899, 362 and 606), forms, in culture liquids, a *diastase* which, like rennet, coagulates casein and casease. The largest amount of casease formed in neutral media, which contain dextrose and peptone, is found when the whole of the dextrose has been assimilated. Casease liquefies gelatin. R. H. P.

Synthetic Action of the Maltase of Yeast. By Oskar Emmerling (*Ber.*, 1901, **34**, 2206—2207).—A reply to Hill (this vol., i, 452). R. H. P.

Contribution to the Study of the Oxydases. By J. Sarthou (*J. Pharm.*, [vi], **13**, 464—465).—Schinoxydase (Abstr., 1900, i, 575), purified by dialysis followed by precipitation by alcohol, contained N, 6·283; S, 0·210; ash (containing iron and calcium), 1·336 per cent. with unweighable traces of phosphorus. This composition suggests that schinoxydase should perhaps be classed with the nucleins. It somewhat resembles an enzyme extracted by Slowtzoff from potato and cabbage, with the difference, however, that the enzyme from potato contains no phosphorus, and acts in a feebly alkaline medium, whilst schinoxydase acts in a neutral one. The author believes that although all the known oxidising enzymes may belong to one group of compounds, they are nevertheless specifically distinct substances, and that for the production of a given phenomenon one of them could not be replaced by another. M. J. S.

***o*-Mercuridibenzoic Acid.** By Leone Pesci (*Atti Real. Accad. Lincei*, 1901, [v], **10**, i, 413. Compare Abstr., 1900, i, 546).—*Sodium* o-*sulphomercuribenzoate*, $S(Hg{\cdot}C_6H_4{\cdot}CO_2Na)_2$, obtained by mixing concentrated solutions of equivalent quantities of sodium *o*-hydroxymercuribenzoate and sodium sulphide, crystallises from alcohol in thin needles. The corresponding *acid* forms a readily decomposable, gelatinous mass. When an aqueous solution of the sodium salt is boiled in a reflux apparatus, mercuric sulphide separates and sodium *o*-mercuridibenzoate is obtained.

o-*Mercuridibenzoic acid*, $Hg(C_6H_4{\cdot}CO_2H)_2$, crystallises from alcohol in shining needles which are insoluble in water and on heating decompose without melting. Its *calcium* salt separates from water in white, mammillary masses. T. H. P.

Organic Chemistry.

Polymerisation of Di*iso*propenyl. By Iwan L. Kondakoff (*J. pr. Chem.*, 1901, [ii], **64**, 109—110. Compare this vol., i, 62).—Di*iso*propenyl is partially polymerised by alcoholic potash (*loc. cit.*). If it is exposed to diffused light for several months, air being excluded, it becomes completely transformed into a white solid, which resembles indiarubber in properties, is insoluble in most solvents, but soluble in benzene, and reacts with bromine, evolving hydrogen bromide. K. J. P. O.

Action of Ethyl Alcohol on Barium Ethoxide. Synthesis of *n*-Butyl Alcohol. By Marcel Guerbet (*Compt. rend.*, 1901, **133**, 300—302. Compare Abstr., 1899, i, 471, 472, and this vol., i, 182, and 307).—*n*-Butyl alcohol is formed when a concentrated (28·5 per cent.) solution of barium ethoxide in ethyl alcohol is heated in sealed tubes at 230—240° for about 3 days, the yield being 3 grams from 500 grams of the ethoxide. J. J. S.

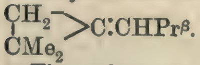
Oxidation of Propylene Glycol by Mycoderma Aceti. By André Kling (*Compt. rend.*, 1901, **133**, 231—233).—Propylene glycol is oxidised by *Mycoderma aceti* in much the same way as by the sorbose bacterium (Abstr., 1899, i, 323; 1900, i, 129), and is converted into acetol, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}OH$. C. H. B.

Isomeric *iso*Butylene Chlorohydrins and the Decomposition of Mixed Ethers by Hydrogen Haloids. By Arthur Michael [and, in part, V. L. Leighton and F. D. Wilson] (*J. pr. Chem.*, 1901, [ii], **64**, 102—109. Compare Abstr., 1900, i, 321).—The chlorohydrin obtained by Butleroff (*Annalen*, 1860, **144**, 125) from *iso*butylene and hypochlorous acid and investigated by Henry (*Bull. Soc. Chim.*, 1876, [ii], **26**, 24), was thought by them to be represented by the formula $CMe_2Cl{\cdot}CH_2{\cdot}OH$. In the case of propylene and hypochlorous acid, the author found (*loc. cit.*) that the hydroxyl group became attached to the carbon atom poorest in hydrogen. *iso*Butylene chlorohydrin boils at 128—129°, and has a sp. gr. 1·0663 at 20°. Since with phosphoric oxide this chlorohydrin yields the two chloro*iso*butylenes $CH_2{:}CMe{\cdot}CH_2Cl$ and $CMe_2{:}CHCl$, it has the formula $OH{\cdot}CMe_2{\cdot}CH_2Cl$. Of the two chloro*iso*butylenes, dimethylchloroethylene is not attacked by boiling alcoholic potash, and represents 75 per cent. of the mixture.

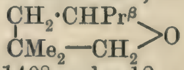
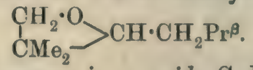
*iso*Butylene oxide yields, with hydrogen chloride, a mixture of two chlorohydrins, $CMe_2Cl{\cdot}CH_2{\cdot}OH$ and $OH{\cdot}CMe_2{\cdot}CH_2Cl$. The mixture boils at 127—130°, and has a sp. gr. 1·0587 at 20°.

The decomposition of mixed ethers by hydrogen haloids, according to Ferreira da Silva (*Ann. Chim. Phys.*, 1875, [v], **7**, 429), results in the halogen becoming attached to the smaller alkyl radicle. The author finds that ethyl propyl ether and hydrogen iodide yield 2 parts of ethyl iodide and 1 part of propyl iodide; propyl *iso*propyl ether both propyl and *iso*propyl iodide, but methyl propyl ether gives only traces of propyl iodide. From these and earlier experiments (*loc. cit.*), the author deduces rules for the decomposition of mixed ethers by hydrogen haloids. K. J. P. O.

Action of Sulphuric Acid on the Glycol from *iso*Butaldehyde and *iso*Valeraldehyde. By VICTOR LÖWY and FRITZ WINTERSTEIN (*Monatsh.*, 1901, **22**, 398—414. Compare Lilienfeld and Taus, Abstr., 1898, i, 508).—When the glycol (Fossek, Abstr., 1891, 31) is heated with 30 per cent. sulphuric acid for 8 hours at 150°, it yields on fractional distillation three liquids boiling respectively at 112°, 140°, and 175° under the ordinary pressure, and a fourth boiling at 140° under 18 mm. pressure. The first of these is a *hydrocarbon*, C_9H_{16}, which does not solidify at $-18°$, with bromine yields a *dibromide*, and on oxidation with aqueous potassium permanganate gives a mixture of *iso*butyric and *iso*valeric acids; its structure is therefore probably



$\begin{matrix}CH_2\\ |\\ CMe_2\end{matrix}\!\!>C{:}CHPr^{\beta}$.

The substance boiling at 140°, $C_9H_{18}O$, does not interact with zinc ethyl and fails to yield an oxime; it is therefore not an aldehyde, but probably an oxide,  $\begin{matrix}CH_2{\cdot}CHPr^{\beta}\\ |\\ CMe_2{-}CH_2\end{matrix}\!\!>O$ or  $\begin{matrix}CH_2{\cdot}O\\ |\\ CMe_2\end{matrix}\!\!>CH{\cdot}CH_2Pr^{\beta}$. The substance boiling at 140° under 18 mm. pressure is an *oxide*, $C_{18}H_{36}O_2$, which is not changed by digesting with water for 10 hours at 100°; it regenerates the parent glycol on heating with 50 per cent. hydrobromic acid for 6 hours at 150°, and boiling the product for 10 hours with aqueous potassium carbonate.

The liquid boiling at 175° is apparently not a pure substance; analyses point to the formula $C_6H_{12}O$, but its molecular weight is about 150—160. It does not interact with either zinc ethyl or acetic anhydride. W. A. D.

Dissociation of the Alkyl Nitrates, Sulphates, and Haloids. By JOHN U. NEF (*Annalen*, 1901, **318**, 1—57. Compare Abstr., 1900, i, 4).—Olefines and mixed ethers are simultaneously produced when the alkyl haloids are treated with sodium ethoxide or alcoholic potassium hydroxide. The formation of the hydrocarbons was formerly assumed to be due to an "alkylene" decomposition, but since the alkyl nitrates and the mono- and di-alkyl sulphates do not yield olefines under these conditions, the author now supposes that, in all cases, the first change is an "alkylidene dissociation," and that if an unsaturated hydrocarbon is liberated, its production is due to a subsequent rearrangement of the alkylidene.

The above generalisation, however, does not hold in the case of a tertiary nitrate, for bromotrimethylcarbyl nitrate, $NO_2{\cdot}O{\cdot}CMe_2{\cdot}CH_2Br$, when treated with alcoholic potassium hydroxide readily yields bromo*iso*crotyl. A study of the interaction of the butyl chlorides and iodides with sodium butyloxide shows that in every case *iso*butylene and an ether are produced; the decomposition of amyl chloride and iodide by sodium ethoxide gives rise to amylene and the mixed ether, and the slower the rate of decomposition the greater is the yield of ether.

n-Propyl sulphate, conveniently prepared by heating propyl iodide, silver sulphate, and ether in sealed tubes at 130°, is an oil boiling at 120° under 20 mm. pressure, and having a sp. gr. 1·11 at 22·5°; it has an agreeable odour, and is only very slowly decomposed by water.

Diisoamyl sulphate, obtained like the preceding ester, boils at 140—145° under 15 mm., and at 145—155° under 20 mm. pressure; the yield in this case is poor owing to a decomposition resulting in the deposition of coke and the formation of sulphurous acid.

Ethyl chloride, when heated at 625°, either alone or in contact with pumice, is completely decomposed into ethylene and hydrogen chloride, but when passed over soda-lime at 350°, it yields hydrogen, methane, water, and ethyl alcohol, but very little ethylene. This difference is explained by assuming that at the lower temperature the chloride undergoes the alkylidene dissociation into hydrogen chloride and ethylidene, $CH_3{\cdot}CH<$, the former product being fixed by the alkali, whilst the latter is successively oxidised by the same reagent into alcohol and acetic acid. Finally, these substances are also decomposed, yielding hydrogen, methane, water, and a carbonate.

Experiments made on the decomposition of the propyl haloids by alcoholic potassium hydroxide solution and by heat alone confirm the view that propylidene changes into the isomeric olefine even more readily than ethylene. Similar decompositions in the *iso*butyl series are assumed to lead to the formation of *iso*butylidene, an alkylidene capable of changing into any one of the three butylenes. *iso*Butyl chloride, when heated at 500° in contact with pumice, dissociates completely into butylene and hydrogen chloride, but the vapours on cooling yield a considerable amount of *tert.*-butyl chloride; a similar result is obtained with *iso*butyl bromide. The three butylenes are formed when these haloids are passed over heated soda-lime, but at temperatures above 600° a certain amount of decomposition occurs, resulting in the formation of hydrogen, methane, and propylene.

The transformation of *iso*amylidene into α- and β-*iso*amylenes is also discussed, and the work of previous investigators on analogous compounds explained on the assumption that in these decompositions an alkylidene is the primary product.

Diethyl sulphate, when heated at 220°, decomposes into ethylidene (2 mols.) and sulphuric acid (1 mol.); about 54 per cent. of the hypothetical hydrocarbon changes into olefine, whilst the remainder interacts with the acid, giving rise to carbon dioxide, sulphur dioxide, water, and carbon. Di-*n*-propyl sulphate decomposes in a similar manner, yielding propylene, &c. Di*iso*amyl sulphate decomposes into trimethylethylene, sulphur dioxide, a tarry product, and a small amount of carbon. Potassium ethyl sulphate, when heated at 250—350°, gives off ethylene, ether, and ethyl alcohol; the *iso*butyl salt gives rise to *iso*butyl alcohol and butylene, and the *iso*amyl salt yields trimethylethylene and *iso*amyl alcohol. In each case, the organic products are accompanied by sulphur dioxide and water. These alkyl sulphates do not furnish olefines when treated with alcoholic potassium hydroxide solution, the sole products under these conditions being the mixed ethers, $C_nH_{2n+1}{\cdot}OEt$. The results are interpreted by assuming that the formation of olefine in the decomposition by heat is due to the production of an alkylidene, and the subsequent transformation of this substance into its stable isomeride.

The phenomenon of etherification is assumed to be due to alkylidene dissociation, and the preparation of ether from alcohol by the agency of sulphuric acid and other dehydrating agents is discussed from the standpoint of this hypothesis. G. T. M.

General Method for Preparing Chlorides of Organic Acids. By Hans Meyer (*Monatsh.*, 1901, 22, 415—442).—The acid is heated with 5—10 times its weight of thionyl chloride, usually at the boiling point of the latter, until completely dissolved; the acid chlorides are generally soluble in the reagent, and can be easily isolated by volatilising the excess of the latter. As only gaseous products (sulphur dioxide and hydrogen chloride) are formed in the action, the method is far preferable to that involving the use of phosphorus pentachloride. *n*-Hexoic, bromoacetic, arachic, and *ικ*-undecenoic acids readily yield their chlorides; *brassic chloride*, $C_{21}H_{41}\cdot COCl$, forms colourless crystals and melts at 14°; *methyl brassate*, $C_{21}H_{41}\cdot CO_2Me$, crystallises from methyl alcohol in large, lustrous leaflets melting at 34—35°. The action of phosphorus trichloride on brassic and erucic acids yields, not the anhydrides as stated by Reimer and Will (Abstr., 1887, 233), but the chlorides of the acids.

Thionyl chloride simply removes the water of crystallisation from oxalic acid, but converts succinic and camphoric acids into the anhydrides; suberic and sebacic acids yield the dichlorides. Maleic, citraconic and itaconic acids give the corresponding anhydrides, but fumaric and mesaconic acids the chlorides. Bromosuccinic acid and malic acid readily yield chlorides, but dibromosuccinic acid is acted on only with difficulty, and then undergoes complex change.

p-Toluic, *o*- and *m*-nitrobenzoic, *o*-chlorobenzoic, *m*-bromobenzoic, phenylacetic, cinnamic, anisic, and veratric acids all readily yield chlorides; from *p*-nitrobenzoic acid a chloride is obtained only with difficulty, and from *p*-bromobenzoic acid not at all. A negative group (NO_2,Br) in the *p*-position thus inhibits the formation of chloride, but a positive group (OMe,Me) has no such influence. *Veratric chloride*, $C_6H_3(OMe)_2\cdot COCl$, forms colourless crystals, melts at 70°, and boils at 275°; *veratramide* forms colourless crystals and melts at 164°.

The chlorides of aromatic hydroxy-acids, which can be obtained only in exceptional cases by the ordinary methods, are as a rule easily prepared by using thionyl chloride. The *o*- and *m*-hydroxy-acids, salicylic, *m*-hydroxybenzoic, *α*- and *β*-cresotic [$CO_2H:Me:OH = 1:2:5$ and $1:2:3$], bromo-*β*-cresotic acid [$CO_2H:Me:OH:Br = 1:3:2:5$], nitro-*β*-cresotic and *α*-resorcylic acids [$CO_2H:(OH)_2 = 1:3:5$] all readily yield chlorides. Only those *p*-hydroxy-acids react, however, which contain a second hydroxyl group in the ortho-position relatively to the first; thus *p*-hydroxybenzoic, *β*-resorcylic [$CO_2H:(OH)_2 = 1:2:4$], and phloroglucinolcarboxylic acids do not yield chlorides, although protocatechuic, gallic, and pyrogallolcarboxylic acids [$CO_2H:(OH)_3 = 1:2:3:4$] readily do so. Terephthalic acid is not acted on by thionyl chloride, but *iso*phthalic acid readily yields a chloride; phthalic acid is converted into the anhydride. 3-Bromo-4-hydroxy- and 3 : 5-dibromo-4-hydroxy-benzoic acids readily yield their chlorides, but vanillic acid gives an indefinite product. α-Hydroxynicotinic acid gives a syrupy chloride, but *o*-coumaric acid undergoes complex decomposition; mandelic acid is remarkable in yielding benzaldehyde only.

Methyl m-*hydroxybenzoate* melts at 57°; *methyl* p-*coumarate* crystallises from methyl alcohol in yellow needles melting at 126°, and *methyl* 1-*hydroxynicotinate* from acetone in colourless plates melting at 164°. W. A. D.

Formation of β-Hydroxy-α-methylbutyric Acid in the Action of Barium Hydroxide on Jalapin. By Nicolai Kromer (*Arch. Pharm.*, 1901, **239**, 373—384).—The product of the action of barium hydroxide on jalapin is acidified, freed from the volatile acids, α-methylbutyric acid, and tiglic acid, by distilling in steam, and then extracted with dry ether, which dissolves two acids. The barium salts of these are separated by alcohol, in which only one is soluble. From the insoluble barium salt, β-hydroxy-α-methylbutyric acid,

$$CHMe(OH){\cdot}CHMe{\cdot}CO_2H,$$

is isolated, and from the soluble barium salt a liquid is obtained which consists of a mixture of 1 part of hydroxymethylbutyric acid and 3 parts of the *ester anhydride*,

$$OH{\cdot}CHMe{\cdot}CHMe{\cdot}CO_2{\cdot}CHMe{\cdot}CHMe{\cdot}CO_2H,$$

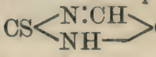
of β-hydroxy-α-methylbutyric acid. This anhydride, on hydrolysis with potassium hydroxide, yields potassium hydroxymethylbutyrate.

Ethyl β-hydroxy-α-methylbutyrate is a liquid boiling at 176—178°. By phosphorus pentachloride it is converted into ethyl tiglate. Hydroxymethylbutyric acid, when heated at 200° or with dilute sulphuric acid, is converted into tiglic acid.

The author believes that α-methylbutyric acid is first formed by the action of barium hydroxide on jalapin; by the further action of barium hydroxide, this is partly converted into hydroxymethylbutyric acid, which in its turn yields tiglic acid. K. J. P. O.

Purgic Acid. By Nicolai Kromer (*Arch. Pharm.*, 1901, **239**, 389—392. Compare preceding abstract).—Purgic acid, obtained by Hoehnel (Abstr., 1897, i, 228) by the action of barium hydroxide on convolvulin, is shown to be a mixture of β-hydroxy-α-methylbutyric acid and its ester anhydride. The former compound is the main constituent of the mixture. K. J. P. O.

Glyoxylic Acid. By Oscar Doebner and G. Glass (*Annalen*, 1901, **317**, 147—156. Compare Abstr., 1900, i, 473).—The metallic glyoxylates, with the exception of the ammonium salt, all contain water of crystallisation, and become anhydrous only after continued heating at 105—110°. These compounds are most conveniently prepared by neutralising a dilute solution of the acid with the corresponding carbonate, the soluble salts being obtained by evaporation at the ordinary temperature. Their solutions cannot be heated, since, with the exception of the calcium compound, the salts are readily decomposed into the corresponding glycollates and oxalates. *Strontium glyoxylate*, $Sr(CHO{\cdot}CO_2)_2,2H_2O$, is stable in the air and resembles the barium salt; the *magnesium* salt, $Mg(CHO\cdot CO_2)_2,3H_2O$, is precipitated by alcohol from its aqueous solution as a white, amorphous, hygroscopic powder. The *aluminium* salt, $Al(CHO\cdot CO_2)_3,H_2O$, is crystalline and soluble; the *nickel* and *cobalt* salts, each with $1H_2O$, are amorphous substances precipitated from their aqueous solutions by alcohol.



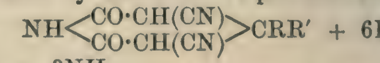
Glyoxylthiocarbamide, $CS<\begin{matrix}N:CH\\NH—\end{matrix}>CO$, obtained by gently heating a mixture of thiocarbamide with a 20 per cent. solution of glyoxylic acid, crystallises from hot water in well-defined, reddish-brown needles and decomposes above 250°; it is sparingly soluble in organic solvents, but dissolves in aqueous solutions of ammonia or sodium hydroxide, yielding a reddish-yellow solution.

β-Naphthaquinoline-1 : 3-dicarboxylic acid is produced by adding a mixture of glyoxylic and pyruvic acids to β-naphthylamine dissolved in hot alcohol (compare Doebner and Peters, Abstr., 1890, 1007); this condensation is a characteristic property of aldehydes, and is supplementary evidence in support of the aldehydic nature of glyoxylic acid. The *silver* salt of the dicarboxylic acid is an insoluble, white powder.

G. T. M.

Compounds of Glyoxylic Acid with Guanidine and Aminoguanidine. By Oscar Doebner and Simon Gärtner (*Annalen*, 1901, 317, 157. Compare this vol., i, 261).—The aminoguanidineglyoxylic acid, $NH:C(NH_2)\cdot NH\cdot NH\cdot CH(OH)\cdot CO_2H$, obtained by the action of glyoxylic acid on aminoguanidine acetate, is identical with the compound prepared by Thiele (Abstr., 1889, i, 7) from chloral and aminoguanidine in aqueous solution, to which he gave the alternative formula, $NH:C(NH_2)\cdot NH\cdot N:CH\cdot CO_2H,H_2O$. G. T. M.

ββ-Dialkylglutaric and γ-Cyano-β-alkylvinylacetic Acids. I. By Icilio Guareschi (*Atti Accad. Sci. Torino*, 1900—1901, 36, 443—458).—The ββ-dialkylglutaric acids may be prepared in practically theoretical yields by hydrolysing the corresponding 3 : 5-dicyano-2 : 6-dioxy-4 : 4-dialkylpiperidines by means of 60 per cent. sulphuric acid, the reaction being:



$NH<\begin{matrix}CO\cdot CH(CN)\\CO\cdot CH(CN)\end{matrix}>CRR' + 6H_2O = CRR'(CH_2\cdot CO_2H)_2 + 2CO_2 + 3NH_3$.

ββ-Dimethylglutaric acid obtained in this way melts at 103—104°; former investigators, who prepared the acid in small quantity, or in a state difficult to purify, give lower temperatures for the melting point.

ββ-Methylethylglutaric acid, $CMeEt(CH_2\cdot CO_2H)_2$, separates from water in anhydrous, colourless needles soluble in alcohol or ether; it melts at 87°, and boils almost unchanged at about 260° under 740 mm. pressure. The *silver* salt is a white, microcrystalline powder stable towards light and almost insoluble in water; the *zinc* salt forms colourless, greasy plates slightly soluble in water, and the *sodium* salt colourless prisms very soluble in water.

ββ-Methylpropylglutaric acid, $CMePr^{\alpha}(CH_2\cdot CO_2H)_2$, crystallises from water in colourless needles melting at 92°, and dissolves in alcohol or ether. Its *zinc* salt forms anhydrous, thin plates sparingly soluble in water.

ββ-Methylbutylglutaric acid, $C_4H_9\cdot CMe(CH_2\cdot CO_2H)_2$, crystallises from water in colourless plates or prisms which melt at 64—65° and are soluble in alcohol or ether. The *silver* salt is obtained as a white, microcrystalline precipitate stable towards light, and the *zinc* salt as colourless needles or plates almost insoluble in water.

[With Edoardo Peano.]—*ββ-Diethylglutaric acid*, $CEt_2(CH_2\cdot CO_2H)_2$, separates from water in shining needles which melt at 108°, volatilise unchanged, and dissolve in alcohol or ether.]

ββ-Ethylpropylglutaric acid, $CEtPr_\alpha(CH_2\cdot CO_2H)_2$, melts at 71—72°. The above acids when neutralised with ammonia or with magnesium hydroxide do not undergo decomposition or yield hydrocarbons.

γ-Cyano-β-methyl-β-butenoic acid (*γ-cyano-β-methylvinylacetic acid*), $CN\cdot CH\colon CMe\cdot CH_2\cdot CO_2H$, obtained by the action of 60 per cent. sulphuric acid on 3-cyano-2 : 6-diketo-4-methyl-Δ^3-tetrahydropyridine or its ammonium derivative, or on 3 : 5-dicyano-2 : 6-diketo-4-methyl-Δ^3-tetrahydropyridine, crystallises from water in needles or large prisms melting at 199—200°. The aqueous solution gives with ferric chloride a brownish-violet colour, whilst with copper acetate it turns yellow and then deposits orange-yellow crystals; by neutralisation with ammonia and addition of silver nitrate, a yellow precipitate is formed which turns reddish, then brown, and finally black.

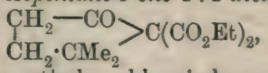
γ-Cyano-β-phenyl-β-butenoic acid (*γ-cyano-β-phenylvinylacetic acid*), $CN\cdot CH\colon CPh\cdot CH_2\cdot CO_2H$, obtained from 3-cyano-4-phenyl-2 : 6-diketo-Δ^5-tetrahydropyridine or from 3 : 5-dicyano-4-phenyl-2 : 6-diketo-Δ^3-tetrahydropyridine, melts at 255—256°.

These results show that, under the experimental conditions employed, a secondary cyano-group is readily hydrolysed, whilst a cyano-group in the tertiary state is attacked either only partially or not at all.

T. H. P.

Synthesis of Derivatives of Dimethyl*cyclo*pentanone, ββ-Dimethyladipic Acid, and αββ-Trimethyladipic Acid. By William Albert Noyes (*J. Amer. Chem. Soc.*, 1901, 23, 392—402).—When heated in sealed tubes with dilute hydrochloric acid, ethyl-2-cyano-3 : 3-dimethyl*cyclo*pentanone-2-carboxylate (Abstr., 1899, i, 929) decomposes into acetic acid, *iso*hexolactone and carbon dioxide, a carbon atom being removed from the ring and replaced by oxygen; in a similar way, hydrolysis with alcoholic potash gives malonic acid and *iso*hexolactone.

Ethyl 2 : 2-*dimethyl*cyclo*pentane*-5-*one*-1 : 1-*dicarboxylate*,



$$\begin{matrix}CH_2\text{—}CO \\ | \\ CH_2\cdot CMe_2\end{matrix}\!\!>C(CO_2Et)_2,$$

prepared by condensing ethyl γ-chloro*iso*hexoate (γ-chloro-γ-methylvalerate) with ethyl malonate, is a nearly colourless oil which boils at 167—169° under 14 mm. pressure, and is hydrolysed by alcoholic, potassium or sodium hydroxide to malonic and hydroxy*iso*hexoic acids.

Triethyl ββ-dimethylbutane-ααδ-tricarboxylate,

$$CO_2Et\cdot CH_2\cdot CH_2\cdot CMe_2\cdot CH(CO_2Et)_2,$$

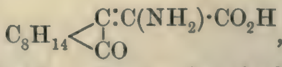
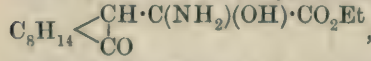
prepared by condensing ethyl chloro*iso*hexoate with ethyl malonate, boils at 150—172° under 15 mm. pressure. The *acid*, $C_9H_{14}O_6$, separates from water in compact crystals, melts and decomposes at 165—175° according to the rate of heating, and is only slightly soluble in cold water. The *calcium* salt, $Ca_3(C_9H_{11}O_6)_2,5H_2O$, is much less soluble in hot than in cold water. *ββ-Dimethyladipic acid*, $CO_2H\cdot CH_2\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CO_2H$, prepared by heating the preceding acid at 200°, crystallises from water in small plates, and melts at 102°; the melting point is 15° higher than that of the dimethyladipic acids described by Tiemann (Abstr., 1898, i, 377) and by Baeyer (Abstr., 1898, i, 676).

αββ-Trimethyladipic acid, $CO_2H\cdot CHMe\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CO_2H$, prepared by heating αββ-trimethylbutane-ααδ-tricarboxylic acid, crystallises from water or from ether in leaflets, melts at 136°, and appears to exist in two modifications.

Methods are described for the preparation of γ-methylvaleric acid, *iso*hexolactone, and γ-chloro-γ-methylvaleric acid. T. M. L.

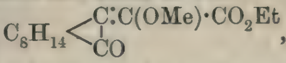
Addition of Bromine to Acetylenedicarboxylic Acid. By WILHELM LOSSEN and A. TREIBICH (*Chem. Centr.*, 1901, ii, 191—192; from *Verh. Vers. Deutsch. Naturforsch. Ärzte*, 1900, ii, 1, 92—93).—The amount of acetylenedicarboxylic acid oxidised to carbon dioxide by bromine is greater the larger the quantity of water present, and when a solution of one part of the acid in 50 of water is used, more than half of the bromine acts in this way. When, however, a solution of the acid is treated very slowly with bromine vapour, the halogen combines with the acid to form additive compounds, $C_4H_2O_2Br_2$, consisting mainly of dibromofumaric acid. E. W. W.

Camphoroxalic Acid Derivatives. VI. By JOHN B. TINGLE (*J. Amer. Chem. Soc.*, 23, 363—391).—A summary is given of previous work on the subject (Trans., 1890, 57, 652; Abstr., 1897, i, 484; 1898, i, 443; 1899, i, 444; 1900, i, 302).

Camphoformeneaminecarboxylic acid,  $C_8H_{14}<\begin{array}{l}C{:}C(NH_2)\cdot CO_2H\\ |\\ CO\end{array}$, prepared by the action of ammonium chloride and potassium hydroxide on a solution in alcohol of camphoroxalic acid, crystallises from benzene or from a mixture of acetone and light petroleum in colourless plates, melts at 178° with liberation of gas, dissolves in sodium carbonate solution only when heated, and is reprecipitated by acids. The *amide*, prepared in a similar manner from ethyl camphoroxalate, crystallises from xylene in colourless, microscopic needles, melts at 227—228°, and appears to give camphoroxalic acid when boiled with aqueous sodium hydroxide; the *platinichloride* crystallises in hexagonal, orange plates. By passing dry ammonia into a solution of ethyl camphoroxalate in ether or absolute alcohol, an additive *compound*, probably  $C_8H_{14}<\begin{array}{l}CH\cdot C(NH_2)(OH)\cdot CO_2Et\\ |\\ CO\end{array}$, is formed as a white precipitate; it gradually decomposes into its constituents, and, when heated at 100° in a sealed tube with alcoholic ammonia, is converted into the amide described above.

Hydroxylamine acts on ethyl camphoroxalate to form a *compound* of unknown constitution, which crystallises from a mixture of toluene and light petroleum in colourless, slender needles, and melts at 120—121°.

Camphoformenemethylaminecarboxymethylamide crystallises from a mixture of benzene and light petroleum in small, white needles and melts at 130°. *Camphoformeneethylaminecarboxyethylamide* crystallises from benzene in colourless needles and melts at 148°.

Ethyl methylcamphoroxalate, 

$C_8H_{14}\textless\begin{matrix}C{:}C(OMe)\cdot CO_2Et\\ |\\ CO\end{matrix}$, prepared by heating ethyl camphoroxalate with silver oxide and methyl iodide, was not obtained in a crystalline form, but the *acid* crystallises from light petroleum in large, hexagonal prisms and plates and melts at 95—96°.

T. M. L.

Condensation of Propaldehyde and Formaldehyde. By HUGO KOCH and THEODOR ZERNER (*Monatsh.*, 1901, **22**, 443—459).—*aa-Dimethylolpropaldehyde*, $CMe(CH_2\cdot OH)_2\cdot CHO$, obtained by leaving propaldehyde and formaldehyde (2 mols.) with aqueous potassium carbonate for 3—4 days at the ordinary temperature, is a slightly yellow, odourless oil which decomposes when distilled at 70—80° in a vacuum, and on reduction yields the pentaglycerol, $CMe(CH_2\cdot OH)_3$ (Hosäus, Abstr., 1893, i, 617). The *oxime* cannot be purified, but, when heated with acetic anhydride for a day, gives the *acetate*, $CN\cdot CMe(CH_2\cdot OAc)_2$, of *aa-dimethylolpropionitrile*, which boils at 145—147° under 14 mm. pressure. The *acetate*, $CMe(CH_2\cdot OAc)_2\cdot CHO$, of the aldol boils at 170—174° under 18 mm. pressure, and gives an *oxime*,

$$CMe(CH_2\cdot OAc)_2\cdot CH{:}N\cdot OH,$$

as a thick, colourless liquid boiling at 169° under 19 mm. pressure and yielding the foregoing nitrile when heated with acetic anhydride. When the nitrile is hydrolysed with hydrochloric acid, it gives acetic acid and *methyldimethylolacetic acid* (*dihydroxypivalic acid*),

$$CMe(CH_2\cdot OH)_2\cdot CO_2H,$$

which crystallises from ether and melts at 163—164°. Alcoholic potash converts *aa*-dimethylolpropaldehyde into a mixture of this acid and the pentaglycerol, $CMe(CH_2\cdot OH)_3$, simultaneous oxidation and reduction occurring as in the case of aromatic aldehydes.

Attempts to prepare the aldol, $CHO\cdot CHMe\cdot CH_2\cdot OH$, by condensing propaldehyde and formaldehyde in molecular proportion gave only *aa*-dimethylolpropaldehyde along with methylethylacraldehyde formed from the excess of propaldehyde. In presence of alcoholic potassium hydroxide, the two aldehydes condense to form the pentaglycerol, $CMe(CH_2\cdot OH)_3$, formic acid, and *ββ-dimethylol-γ-pentanol*,

$$CMe(CH_2\cdot OH)_2\cdot CH(OH)\cdot CH_2Me\ ;$$

this boils at 135—137° under 15 mm. pressure, and yields a *triacetyl* derivative, $C_{13}H_{22}O_6$, boiling at 136° under 14 mm. pressure.

W. A. D.

Conversion of Pyrrole into the Tetramethylacetal of Succindialdehyde. By CARL D. HARRIES (*Chem. Centr.*, 1901, ii, 307, from *Verh. Vers. Deutsch. Naturforsch. Ärzte*, 1900, ii, 1, 87—89).—Succintetramethylacetal (Abstr., 1898, i, 232) may be obtained by cooling a rather dilute solution of succindialdoxime (Abstr., 1885, 246; 1889, 1208; 1890, 1155) in methyl alcohol containing sufficient hydrogen chloride to form hydroxylamine hydrochloride (2 mols.). When the solution is treated with absolute ether, hydroxylamine hydrochloride and salts of other organic bases are precipitated, and the filtrate, after removal of hydrogen chloride by silver oxide and evaporation, yields an oil which contains an imino-ether of the semi-acetal of succinic acid, $CH(OMe)_2\cdot CH_2\cdot CH_2\cdot C(OMe){:}NH$, and ethylenedi-imino-ether, $C_2H_4[C(OMe){:}NH]_2$.

Succintetramethylacetal, $C_2H_4[CH(OMe)_2]_2$, obtained by removing the bases contained in the oil by saturating its ethereal solution with hydrogen chloride, is a stable oil, has an odour like that of paraldehyde, boils at 82—84° under 14 mm., and at 182—185° under the ordinary pressure, and is easily volatile in steam or alcohol or ether vapour. *Succindialdehyde*, prepared by the action of dilute hydrochloric acid on the tetramethylacetal at 80°, is a colourless oil, has an extremely pungent odour resembling that of heptaldehyde, boils at about 62—65° under 12 mm. pressure, readily reduces Fehling's solution in the cold, gives the pyrrole reaction with ammonia and acetic acid, and with hydroxylamine hydrochloride forms the dialdoxime.

E. W. W.

Constitution of, and Action of Aqueous Ammonia on, Sodium Cellulose. By EDMUND THIELE (*Chem. Zeit.*, 1901, **25**, 610—612).—Various formulæ have been used to express the empirical constitution of the compound formed by the action of concentrated solutions of sodium hydroxide on cellulose (cotton). The action of aqueous ammonia on "mercerised" cotton has been studied by the present author, and from the quantitative results the formula $C_{12}H_{20}O_{10},2NaOH$ is established for the sodium cellulose. Mercerised cotton is not "demercerised" by ammonia, as it remains elastic and is apparently converted into a hydrate of cellulose, which differs from the inelastic hydrate obtained by treating mercerised cotton with water.

R. H. P.

Action of Ammonia on Amine Hydrochlorides. By FÉLIX BIDET (*Compt. rend.*, 1901, **133**, 238—239).—Dry ammonia is absorbed by dry ethylamine hydrochloride with liberation of the amine and formation of ammonium chloride, the limiting pressure being 340 mm. at 0°, 462 mm. at 9·8°, and 555 mm. at 16·6°. Diethylamine hydrochloride behaves similarly, but the limiting pressures are much higher, being 891 mm. at 0°, 1167 mm. at 9·5°, and 1301 mm. at 13·5°.

C. H. B.

Aliphatic *iso*Cyanides and Nitro-compounds. By FELIX KAUFLER and CÆSAR POMERANZ (*Monatsh.*, 1901, **22**, 492—496).—Dimethyl sulphate interacts vigorously with concentrated aqueous potassium cyanide at 0°, yielding 75 per cent. of acetonitrile and 25 per cent. of the *iso*cyanide. When potassium nitrite is used, 25 per cent. of the product is nitromethane, the rest being methyl nitrite. Under non-dissociating conditions, the action of the potassium salt takes place mostly by addition, and yields an *iso*cyanide or nitro-compound, as in the case of the silver salts; thus, $AgCN + MeI = AgCN{:}MeI \longrightarrow AgI + C\vdots NMe$. Where dissociation can occur, the ions of the potassium salt are active, and give rise to a nitrile or a nitrite, for example, $\overset{+}{\mathrm{K}}\overset{-}{\mathrm{CN}}+\mathrm{MeI}=\overset{+}{\mathrm{K}}\mathrm{I}+\mathrm{MeCN}$. W. A. D.

Action of Hypophosphorus Acid on Acetone. By CH. MARIE (*Compt. rend.*, 1901, **133**, 219—221).—The prolonged action of glacial hypophosphorus acid on boiling acetone yields a monobasic *acid*, $C_6H_{15}O_4P$, which melts and decomposes at 180—181°, forms large, lamellar crystals seemingly belonging to the monoclinic system, decomposes carbonates, and yields crystallisable salts. There are formed at the same time, another crystallisable monobasic *acid*, $C_3H_9O_3P$, which melts at 40—41°, decomposes carbonates, and forms non-crystallisable alkali-salts and a soluble and crystalline lead salt, and a dibasic *acid*, $C_3H_9O_4P$, which melts and decomposes at 169—170°, and forms an insoluble lead salt. C. H. B.

Ammonio-compounds of Cupric and Cuprous Thiocyanates. By FRANZ M. LITTERSCHEID (*Arch. Pharm.*, 1901, **239**, 336—340. Compare Schmidt and Malmberg, Abstr., 1898, i, 547).—The author prepares ammonio-cupric thiocyanate, $Cu(NH_3{\cdot}CNS)_2$, by adding ammonium thiocyanate and dilute ammonia to a solution of copper sulphate (compare Meitzendorff, *Ann. Phys. Chem.*, 1842, **56**, 85). By use of concentrated solutions, or treatment of the ammonio-cupric compound just mentioned with concentrated ammonia, a *compound*,

$$Cu(NH_3,CNS)_2,2NH_3,$$

is obtained as lustrous, dark blue, rhombic plates which slowly evolve ammonia.

Cuproso-cupric thiocyanate does not combine with ammonia, but yields ammonio-cupric thiocyanate. K. J. P. O.

Action of Sunlight on Aqueous Solutions of Potassium Ferrocyanide. By J. MATUSCHEK (*Chem. Zeit.*, 1901, **25**, 565—566. Compare this vol., i, 455 and 584).—Aqueous solutions of potassium ferrocyanide decompose in sunlight according to the equation: $4KCN,2Fe(CN)_2+6H_2O=Fe_2(OH)_6+6KCN+6HCN$. The amount of ferric hydroxide formed increases in arithmetical progression as the concentration of the solution decreases. R. H. P.

Action of Sulphur Dioxide on [Aqueous Solutions of] Potassium Ferrocyanide. By J. MATUSCHEK (*Chem. Zeit.*, 1901, **25**, 612. Compare following abstract).—Berlin blue is formed by the action of sulphur dioxide on aqueous potassium ferrocyanide only in direct sunlight and in the presence of air. R. H. P.

Action of Sulphur Dioxide on Aqueous Solutions of Potassium Ferricyanide. By J. MATUSCHEK (*Chem. Zeit.*, 1901, **25**, 587—588).—An aqueous solution of potassium ferricyanide in the absence of light is not altered by a stream of sulphur dioxide, but in the presence of light is decomposed with the formation of Berlin blue in accordance with the equation, $7[Fe_2(CN)_6,6KCN]+21SO_2+24H_2O=2Fe_4[Fe(CN)_6]_3+21K_2SO_3+48HCN+3O$, the hydrogen cyanide in the presence of an excess of sulphur dioxide being converted into formic acid. R. H. P.

Comparative Experiments on the Intensity of the Action of Light on Aqueous Solutions (containing Equal Amounts of Iron) of Potassium Ferrocyanide and Ferricyanide. By J. MATUSCHEK (*Chem. Zeit.*, 1901, **25**, 601. See this vol., i, 455 and 584).—Aqueous solutions of potassium ferricyanide are decomposed with the formation of ferric hydroxide by light quicker than solutions of potassium ferrocyanide containing the same amount of iron. In the case of the ferricyanide, traces of Berlin blue are formed in amounts which increase with the concentration of the solution and the consequent decrease in the amount of ferric hydroxide formed.

R. H. P.

Additive Reactions of Thiol Acids. By HENRY L. WHEELER [and, in part, BAYARD BARNES and WILLIAM VALENTINE] (*J. Amer. Chem. Soc.*, 1901, **23**, 443—449. Compare Abstr., 1900, i, 563, 564, 632, and this vol., i, 514).—Phenylthiocarbimide and thiobenzoic acid readily form an additive product, *benzoylthiolcarbanilic acid*, NBzPh·CO·SH, which crystallises in colourless needles melting and decomposing at 97—99°, and on heating is converted into carbonyl sulphide and benzanilide. Diphenylformamidine and thiobenzoic acid form an additive *product*, $C_{20}H_{18}ON_2S$, which crystallises in colourless needles, melts at 145—150°, and when heated yields thioformanilide and benzanilide. The additive *product*, $C_{20}H_{18}ON_2S$, from phenylbenzenylamidine and thiobenzoic acid, crystallises in yellowish-white needles melting at 141—142°. Phenyl-*p*-tolylbenzenylamidine and the thiol acid yield a *compound*, $C_{27}H_{24}ON_2S$, as a yellow precipitate melting at 131—132°. Benziminon-*n*-propyl ether and thiobenzoic acid give a very unstable compound, which, on warming, decomposes into benzamide and n-*propyl thiolbenzoate*, which is an oil boiling at 251—255°.

These additive products are analogous to that formed from benzylideneaniline and thioacetic acid (Eibner, this vol., i, 321). The author believes that the addition of the thiol acid to the group $\vdots C \vdots N-$ takes place in two different ways. Thus, in the case of thiobenzoic acid and phenyl thiocarbimide, the benzoyl group becomes attached to the nitrogen, and the compound is represented by the formula previously given, whilst with the amidines the additive compound is best represented by the formula $NH_2\cdot CR(NH_2)\cdot SBz$.

No additive product but only phenylacetamide was obtained from phenylacetiminomethyl ether and thiobenzoic acid. Acetonephenylhydrazone and thiobenzoic acid gave benzoylphenylhydrazine and some dibenzoylphenylhydrazine.

Diisobutylamine thiolbenzoate, $NH(C_4H_9)_2,SHBz$, prepared from *iso*butylamine and thiobenzoic acid, crystallises in flattened prisms melting at 124°.

Methyl alcohol reacts with thiobenzoic acid, producing methyl benzoate; the reaction of the acid with phenol is much slower.

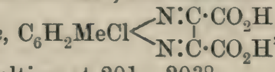
K. J. P. O.

Dichlorinated *o*-Xylenes. By LUCIEN FERRAND (*Compt. rend.*, 1901, **133**, 169—171).—On passing chlorine into cold *o*-xylene containing 1 per cent. of iodine and 10 per cent. of *m*-xylene as an impurity, a solid, melting at 68·5—72°, and two liquids, boiling respectively at

226—228° and 229—231·5°, are obtained (compare Claus and Kantz, Abstr., 1885, 972; 1890, 1247). The solid is a mixture of 3 : 4-*dichloro-o-xylene* and dichloro-*m*-xylene; both liquids are mixtures of 4 : 5- and 3 : 6-dichloro-*o*-xylenes and dichloro-*m*-xylene. This was established by studying the phthalic acids formed on oxidation with dilute nitric acid; 3 : 4-*dichloro-o-phthalic anhydride* sublimes in white needles, melts at 185—186°, yields a *phthalimide* melting at 219°, and a *phenylimide* melting at 209°; 3 : 4-*dichloroanthranilic acid* melts at 183°.

W. A. D.

Chlorination of *o*-Nitrotoluene. By Paul Cohn (*Monatsh.*, 1901, **22**, 473—491).—Under Janson's conditions (Germ. Pat. 107505), the principal product of the chlorination of *o*-nitrotoluene is 6-chloro-2-nitrotoluene, but a considerable amount of the 4-chloro-2-nitro-compound is also formed; this was shown in two ways. (1) The product was oxidised to chloronitrobenzoic acid and esterified; the 6-chloro-2-nitrobenzoic acid, according to V. Meyer's rule, did not yield an ester, but considerable quantities of the isomeric ethyl 4-chloro-2-nitrobenzoate were formed. (2) The chlorination product was reduced to chlorotoluidine, acetylated and oxidised by potassium permanganate; a 4-chloroanthranilic acid was isolated from the product.

6-*Chloro*-2 : 3-*dinitrotoluene*, obtained by the nitration of 6-chloro-2-nitrotoluene with a mixture of nitric and sulphuric acids at 0°, crystallises from alcohol in nearly white, rhombic plates [$a : b : c = 1 : 0·667 : 1·05$] and melts at 106°; the relatively ortho-position of the two nitro-groups follows from the fact that no action occurs on boiling the substance with potassium hydroxide or aniline, and that on reduction a *diamine* is formed which crystallises from a mixture of light petroleum and benzene, melts at 46—47°, and combines with dihydroxytartaric acid to form an *azine*,  $C_6H_2MeCl<\begin{array}{l}N{:}C\cdot CO_2H\\ \quad\vert\\ N{:}C\cdot CO_2H\end{array}$, crystallising in slender, white needles, and melting at 201—203°.

Pure 6-chloro-*o*-toluidine boils at 242—244°; its acetyl derivative melts at 157° [Hönig (Abstr., 1887, 1034) gives 136°]; the *hydrochloride* forms silvery, lustrous leaflets, and decomposes at 250—252°; the *sulphate* is similar and decomposes at the same temperature; the *platinichloride, nitrate*, and *oxalate* are also described. The *benzoyl* derivative crystallises from alcohol in lustrous needles, and melts at 170—171°.

The structure of 4-chloro-*o*-toluidine (m. p. 140°) was determined by oxidising its acetyl derivative with aqueous potassium permanganate in presence of magnesium sulphate to 4-*chloro*-2-*acetylaminobenzoic acid*, $CO_2H\cdot C_6H_3Cl\cdot NHAc$, which crystallises from dilute alcohol in bright brown needles, melts at 235—236°, and yields 2 : 4-dichlorobenzoic acid through the diazo-reaction.

6-Chloroacetyl-*o*-toluidide, on similar oxidation, yields 6-*chloro*-2-*acetylaminobenzoic acid*, which crystallises from water in white, lustrous needles and melts at 215°; 6-*chloro*-2-*aminobenzoic acid*, $NH_2\cdot C_6H_3Cl\cdot CO_2H$, crystallises from benzene in slender, yellowish-white needles, melts at 146—147°, and yields a *hydrochloride* which forms long, white needles and melts and decomposes at 195°. It is converted by the diazo-reaction into 2:6-dichlorobenzoic acid (m. p. 133—134°).

On reduction with zinc dust and sodium hydroxide, 6-chloro-2-nitrotoluene yields, along with 6-chloro-*o*-toluidine, *oo-dichloroazotoluene*, and *oo*-dichlorotolidine [Cl : Me : NH_2 = 2 : 3 : 4, German Patents 82140 and 97101]; the former crystallises from benzene in orange-red, prismatic needles and melts at 153—154°, the latter softens at 192°, melts at 197°, and yields a crystalline *hydrochloride* and *sulphate*. W. A. D.

Tervalent Carbon. By MOSES GOMBERG (*J. Amer. Chem. Soc.*, 1901, **23**, 496—502. Compare this vol., i, 77, 198, 374).—When zinc is allowed to act on triphenylchloromethane in the presence of ether (*loc. cit.*), a dark, viscous mass separates, together with white crystals. The former is a compound of triphenylchloromethane and zinc chloride. Using benzene as solvent, the same substance is precipitated ; in the presence of ethyl acetate, it is not formed, as it is soluble in this solvent. It is most readily prepared by adding a solution of zinc chloride in ether to a solution of triphenylchloromethane in benzene. This additive compound could not be obtained in a crystalline state, but a number of other crystalline compounds of triphenylchloromethane and metallic chlorides have been prepared, and will be described later.

The white crystals are a *compound* of triphenylmethyl and ether, $2CPh_3,Et_2O$, and do not lose ether when kept in an exhausted desiccator over sulphuric acid. The similar crystals obtained when ethyl acetate is the solvent are a *compound* of triphenylmethyl and ethyl acetate, $2CPh_3,CH_3\cdot CO_2Et$; this substance is more stable than the ether compound. The author suggests for the ether compound the formula $Et_2O\colon(CPh_3)_2$, in which oxygen is quadrivalent. K. J. P. O.

New Method for preparing Aniline and Analogous Bases. By PAUL SABATIER and JEAN BAPTISTE SENDERENS (*Compt. rend.*, 1901, **133**, 321—324).—Nitrobenzene is quantitatively transformed into aniline by passing its vapour, mixed with hydrogen, over copper reduced from its oxide and heated at 300—400°. No change in the metal occurs. *o*- and *m*-Nitrotoluenes yield pure toluidines in a similar manner.

Freshly reduced nickel is similar, but more vigorous in its action ; at 200°, the action is normal, but at 250°, benzene, *cyclo*hexane, and ammonia, as well as aniline, result from nitrobenzene. At 300°, benzene is the principal product, and if the hydrogen is in great excess methane is also formed ; above 300°, in presence of little hydrogen, aniline, benzene, ammonia, and diphenylamine are produced, the last-named base being formed by the action of the nickel on the aniline.

Iron, reduced from its oxide at 450—500°, and cobalt act like nickel ; platinum black is very similar in its action to copper, no ammonia being formed, but in presence of little hydrogen some hydrazobenzene is produced.

Water-gas can be used instead of hydrogen with copper at 300—400°, and nickel at 200—230°, and the same is true of coal gas purified by passage over heated copper turnings. W. A. D.

Limits of Combination in Tertiary Amines. By EDGAR WEDEKIND (*Annalen*, 1901, **318**, 90—116. Compare Abstr., 1900, i, 155, and this vol., i, 216).—On treating dimethylaniline with a series of alkyl iodides, it is found that the yield of quaternary iodide rapidly diminishes as the homologous series is ascended, the proportions of the compounds NMe_3PhI and NMe_2EtPhI obtained being 89 and 16 per cent. respectively. Methyl iodide and benzyl iodide have similar capacities for addition, the yield of quaternary salt from the latter compound being 83 per cent. The substitution of a branched chain derivative for its normal isomeride greatly diminishes the capacity for combination, the yield of *n*-propyl salt being 28 per cent., whilst that of the *iso*propyl compound is only about 5; a similar result is observed in the case of the butyl quaternary iodides. Allyl iodide is the most reactive of the haloid ethers under investigation, the yield of the compound $C_3H_5 \cdot NMe_2PhI$ being about 93 per cent.

The facility with which any given quaternary iodide may be prepared depends entirely on the order in which the radicles are introduced; thus, only a 15 per cent. yield of the salt NMe_2EtPhI is obtained by treating dimethylaniline with ethyl iodide, whereas the reaction between ethylmethylaniline and methyl iodide is quantitative. Methyl iodide reacts with di*iso*propyl- and di*iso*amyl-anilines, giving yields of about 45 per cent. *iso*Propyl and *iso*amyl iodides, on the other hand, exhibit very little tendency to combine with dimethylaniline, the yield in each case being less than 3 per cent. Any asymmetric quaternary iodides may be formed from the corresponding tertiary bases in three different ways, each mode of combination having a different velocity of reaction. Ethylallylaniline readily combines with benzyl iodide to yield the quaternary salt, $CH_2Ph \cdot NEtPhI \cdot C_3H_5$, but does not react with benzyl bromide, so that the iodide just falls within the limits of the base's capacity for combination.

Although triethylamine forms a dibromide, it is not possible to obtain compounds of the type $NEt_3Cl \cdot CO \cdot R$ by treating this base with an acid chloride.

When triethylamine is treated with benzoyl or acetyl chloride, the hydrochloride of the tertiary base is produced, and in the latter experiment dehydracetic acid is simultaneously formed in accordance with the following equation, $4AcCl + 4NEt_3 = 4NEt_3,HCl + C_8H_8O_4$; triethylamine hydrochloride is also formed by the action of phenylacetyl chloride on the tertiary base. Benzylpiperidine reacts with ethyl chlorocarbonate, and triethylamine and other tertiary bases yield crystallisable additive compounds with the alkyl esters of the haloid acetates.

Methyl triethylammoniumiodoacetate, $NEt_3I \cdot CH_2 \cdot CO_2Me$, prepared by mixing triethylamine with methyl iodoacetate at the ordinary temperature, crystallises from acetone in lustrous, monoclinic prisms, and melts and decomposes at 138—139°.

Ethyl benzylpiperidiniumchloroacetate,

$$C_5NH_{10}Cl(CH_2Ph) \cdot CH_2 \cdot CO_2Me,$$

obtained by warming benzylpiperidine and methyl chloroacetate for 4 hours on the water-bath, crystallises from chloroform or benzene in colourless needles and melts at 193—194°. The corresponding *bromo-*

acetate is produced either by heating together benzylpiperidine and ethyl bromoacetate, or by adding benzyl bromide to ethyl piperidylacetate; it melts and decomposes at 133—134°. *iso*Propylpiperidine and ethyl bromoacetate also yield a crystalline, additive product.

Methyl quinoliniumiodoacetate, $C_9NH_7I{\cdot}CH_2{\cdot}CO_2Me$, produced by mixing its generators at the ordinary temperature, crystallises from alcohol in reddish-brown needles and decomposes at 151—152°. On treating an aqueous solution of methyl benzylpiperidiniumiodoacetate with silver oxide, a small quantity of a compound is produced which is probably *benzylpiperidiniumhydroxyacetate*,

$$OH{\cdot}C_5NH_{10}(CH_2{\cdot}Ph){\cdot}CH_2{\cdot}CO_2H;$$

it crystallises in rhombic prisms.

Dimethylaniline and ethyl iodoacetate combine, yielding *ethyl phenyldimethylammoniumiodoacetate*, a compound crystallising in silvery leaflets and melting at 126—127°; diethylaniline under these conditions yields only a tarry product.

Methyl methyltetrahydroquinoliniumiodoacetate,

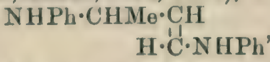
$$C_9NH_{10}MeI{\cdot}CH_2{\cdot}CO_2Et,$$

obtained from kairoline and ethyl iodoacetate, crystallises from acetone in yellowish, monoclinic prisms and melts at 118—119°; it is accompanied by an isomeride separating in rhombohedral crystals and melting at 167—169°. The former compound is the normal product, and can be produced by the addition of methyl iodide to *ethyl tetrahydroquinolylacetate*, $C_9H_{10}N{\cdot}CH_2{\cdot}CO_2Et$; the latter substance is prepared by heating tetrahydroquinoline with ethyl chloroacetate on the water-bath; it is an oil boiling at 180—190° under 17 mm. pressure, and having decidedly basic properties.

Kairoline, when treated with methyl iodoacetate, yields two products, melting respectively at 150—155° and 164—166°. The substance of lower melting point is the normal *methyl tetrahydroquinoliniumiodoacetate*; it is also prepared by the action of methyl iodide on *methyl tetrahydroquinolylacetate*, an oil boiling at 170—190° under 13 mm. pressure, prepared by the action of ethyl chloroacetate on tetrahydroquinoline. The nature of the by-products obtained by the action of alkyl iodoacetates on kairoline has not been determined.

G. T. M.

The Supposed Existence of Miller and Plöchl's Stereoisomeric Anil Compounds [Constitution of Eckstein's Ethylideneaniline]. By ALEXANDER EIBNER (*Annalen*, 1901, **318**, 58—89. Compare Abstr., 1899, i, 41).—Ethylideneaniline (m. p. 126°), the stable base obtained by the condensation of aniline and acetaldehyde (Eckstein, Abstr., 1892, 1191), is now considered to have the structural formula



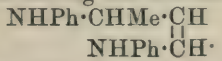
$$\begin{array}{l} NHPh{\cdot}CHMe{\cdot}CH \\ \qquad\qquad\quad\;\, \| \\ \qquad\qquad\quad H{\cdot}C{\cdot}NHPh \end{array}$$

, and the following experimental data confirm this view of its constitution.

The *hydrochloride*, $C_{16}H_{18}N_2,2HCl$, and the *nitrate*, $C_{16}H_{18}N_2,2HNO_3$, are stable, colourless salts, crystallising respectively in lustrous prisms and aggregates of needles. The *diacetyl* derivative crystallises from alcohol in highly refractive prisms and melts at 188°. The monobenzoyl derivative yields the *nitrosoamine*, $C_{23}H_{21}O_2N_3$, on treatment with nitrous acid; this product crystallises from ether in amber-coloured prisms and melts at 147·5°. The nitrosoamine gives Liebermann's reaction, and when treated at the ordinary temperature with alcoholic hydrochloric acid becomes transformed into the isomeric *nitroso*-compound; this substance closely resembles nitrosodimethylaniline and melts at 217°. Eckstein's base is not reduced by sodium and amyl alcohol, and does not combine with hydrogen cyanide. These results all point to the existence of two aniline residues (NHPh–) in the compound.

The existence of the olefine linking is demonstrated by the behaviour of the monobenzoyl derivative towards bromine; this compound readily takes up 1 mol. of bromine in chloroform solution, and yields the *dibromide*, $C_{23}H_{22}ON_2Br_2$, a substance crystallising in lustrous leaflets and melting at 218°. Two products melting respectively at 179·5°, and 156°, are obtained by the action of bromine on the diacetyl compound, but these substances are still under investigation.

The labile isomeride of Eckstein's base (m. p. 85°), discovered by Eibner (Miller and Plöchl, Abstr., 1894, i, 410), is considered to be a stereoisomeric modification having the constitution



$$\begin{array}{r}\mathrm{NHPh{\cdot}CHMe{\cdot}CH}\\ \| \\ \mathrm{NHPh{\cdot}CH{\cdot}}\end{array}$$

Both substances yield benzylidenequinaldine and benzylaniline when heated with benzaldehyde, but the reaction takes place more readily in the case of the *cis*-modification.

The *trans*-base may be distilled without decomposition, whereas the *cis*-isomeride, on heating, decomposes into quinaldine, aniline, and hydrogen; moreover, it is readily converted into the stable compound by the action of a trace of iodine. The stable base may also be prepared either by condensing aniline (2 mols.) with aldol or paraldol, or by warming aldol-aniline with a further quantity of the base.

The higher homologues of Eckstein's base yield *dinitrosoamines* with very dilute alcoholic solutions of nitrous acid, that from Wormser's base, ethylidene-*p*-toluidine (m. p. 116°), crystallises in yellow needles and melts at 156°, and the corresponding derivative of Sender's base, propylideneaniline (m. p. 103°), forms yellow prisms melting at 135°.

The base obtained from acetaldehyde and *as.*-*m*-xylidine (Mozdzynski Abstr., 1895, i, 534) yields a pale yellow, amorphous *nitrosoamine.*

G. T. M.

Condensation of *iso*Butaldol with Aniline. By Ernst Friedjung and Gustav Mossler (*Monatsh.*, 1901, **22**, 460—472).—The condensation of *iso*butaldol with aniline in presence of a saturated potassium carbonate solution gives a mixture of the *dianil*, $CHPr^{\beta}(NHPh)_2$, of *iso*butaldehyde and the *anil*, $OH{\cdot}CHPr^{\beta}{\cdot}CMe_2{\cdot}CH{:}NPh$, of the aldol. The former boils at 86—87° under 18 mm. pressure, is slowly oxidised in the air to hydrazobenzene and *iso*butaldehyde, and by alkaline potassium permanganate to azobenzene and *iso*butyric acid; the latter boils at 106—109° under 18 mm. pressure, and is resolved by warm dilute mineral acids into aniline and the aldehyde, instead of yielding a quinoline derivative.

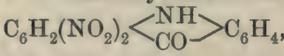
The action of aniline on *iso*butaldehyde (compare Miller, Plöchl, and Lettenmayer, Abstr., 1892, 1192) yields a mixture of the dianil,

$CHPr^{\beta}(NHPh)_2$, and the *anil*, $CHPr^{\beta}:NPh$, which boils at 95° under 18 mm. pressure; a considerable quantity of hydrazobenzene is also formed. W. A. D.

New Diphenylamine Derivatives. By PAUL COHN (*Monatsh.*, 1901, **22**, 385—397).—The dinitrochlorobenzoic acid of the German Patent 106510 yields 3 : 5-dinitro-2-aminobenzoic acid when boiled with an excess of aqueous ammonia, and 3 : 5-dinitrosalicylic acid when heated with aqueous sodium hydroxide for 6 hours; its structure is therefore $CO_2H : Cl : (NO_2)_2 = 1 : 2 : 3 : 5$. The *ethyl* ester crystallises from light petroleum in long, yellowish plates and melts at 54°.

The following compounds were obtained by condensing the acid with various bases. 2 : 4-*Dinitrodiphenylamine*-6-*carboxylic acid*, prepared by using aniline, crystallises from dilute alcohol in yellow needles and melts at 214°; the *sodium* salt forms dark yellow, and the *potassium* salt red needles, the *calcium* salt orange-yellow, and the *barium* salt yellow plates; the *ammonium* salt is monoclinic

$$[a : b : c = 1{\cdot}9337 : 1 : 1{\cdot}9227 : \beta = 107^{\circ}{\cdot}67']$$

The *acetyl* derivative forms yellow needles and melts at 209—210°; the *benzoyl* derivative is microcrystalline and melts at 120—121°. 1 : 3-*Dinitroacridone*,  $C_6H_2(NO_2)_2{<}\begin{smallmatrix}NH\\CO\end{smallmatrix}{>}C_6H_4$, obtained by heating the acid with concentrated sulphuric acid for 5 hours at 100°, crystallises from pyridine in lustrous scales and does not melt at 300°.

2 : 4-*Dinitro*-4′-*hydroxydiphenylamine*-6-*carboxylic acid*, obtained by using *p*-aminophenol (German Patent 108872), forms lustrous, dark red needles, melts at 103°, and yields a red, microcrystalline, *sodium* salt; the *potassium* salt forms stellate aggregates of red needles, and the *ammonium* salt, red, six-sided plates; the *barium* salt is deliquescent. The *acetyl* derivative crystallises from water in red needles melting at 97—99°, and the *benzoyl* derivative in yellow needles melting at 123°.

2 : 4-*Dinitrophenyl*-α-*naphthylamine*-6-*carboxylic acid*, obtained by using α-naphthylamine, crystallises from dilute alcohol in lustrous, red needles, and melts at 150—151°; the *sodium* and *potassium* salts form orange-red needles, and the *ammonium* salt is microcrystalline. The *acetyl* derivative is easily soluble in alcohol, and the *benzoyl* derivative crystallises in small, red needles.

2 : 4-*Dinitrophenyl*-β-*naphthylamine*-6-*carboxylic acid* crystallises from dilute alcohol in microscopic, orange-red needles and melts at 238—239°; the *sodium* and *potassium* salts crystallise in orange-red plates, and the *ammonium* salt in lustrous, red, four-sided plates. The *acetyl* derivative is very soluble in alcohol, whilst the *benzoyl* derivative crystallises in lustrous, orange-yellow needles, melting above 300°.

2 : 4-*Dinitrodiphenylamine*-6 : 6′-*dicarboxylic acid*, obtained by using anthranilic acid, crystallises from dilute alcohol in yellowish-brown, lustrous needles, sinters at 135° and melts between 153° and 159°. The *alkali* salts are very soluble in water, the *calcium* salt is a crystalline precipitate, and the *barium* salt forms small, orange needles. The *acetyl* derivative forms small, yellow needles and melts at 254—255°. W. A. D.

Phenacylphenacetin. By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1901, **25**, 628).—*Phenacylphenacetin*, $OEt\cdot C_6H_4\cdot NAc\cdot CH_2\cdot COPh$, obtained by the action of bromoacetophenone on sodium phenacetin, is a crystalline substance melting at 87°, is soluble in alcohol and glycerol but insoluble in water, is not poisonous, and acts as a hypnotic antipyretic.

Triphenylguanidine guaiacolsulphonate, obtained by the action of triphenylguanidine sulphate on barium guaiacolsulphonate, crystallises in leaflets, melts at 50° and can be used as a local anæsthetic.

R. H. P.

[Ethers and Esters of 2:4-Di-iodo- and 2:4:6-Tri-iodophenol.] By P. BRENANS (*Compt. rend.*, 1901, **133**, 160—162).—The following ethers were prepared from 2 : 4-di-iodo- and 2 : 4 : 6-tri-iodophenol by heating them with the alkyl iodide and alcoholic potassium hydroxide, and the esters by interaction with the acid chlorides.

From 2 : 4-di-iodophenol :—The *propyl* ether crystallises from benzene in lamellæ melting at 32°, the *iso*propyl ether boils at 235—237° (corr.) under 77 mm. pressure, and the *allyl* ether at 110—112° under 139 mm. pressure. The *benzoate* crystallises from acetic acid and light petroleum in slender, flattened needles and melts at 96—97° ; the *succinate* forms prisms melting at 209°, and the *phthalate* needles melting at 153°.

From 2 : 4 : 6-tri-iodophenol :—The *methyl* ether crystallises from light petroleum in colourless spangles, from ether in long needles, and melts at 98—99° ; the *ethyl* ether forms long, colourless needles melting at 83° ; the *propyl*, *allyl*, and *benzyl* ethers separate in needles and melt respectively at 81°, 113—114°, and 123°. The *acetate* crystallises from light petroleum in needles or triclinic prisms melting at 156° ; the *benzoate* crystallises from benzene in large prisms and melts at 137°.

W. A. D.

Pyrogallolsulphonic Acids. By MARCEL DELAGE (*Compt. rend.*, 1901, **133**, 297—299. Compare Abstr., 1900, i, 595, and this vol., i, 274).—When phenolphthalein is used as indicator, pyrogallolmonosulphonic acid reacts as a dibasic acid and the disulphonic acid as a tribasic acid, owing to the acidic function of one of the OH groups.

Potassium pyrogallolsulphonate, $C_6H_5O_3\cdot SO_3K,2H_2O$, forms large, transparent crystals readily soluble in water ; the *sodium* salt, with $2H_2O$, and the *ammonium* salt, with $1H_2O$, crystallise in colourless prisms and needles.

Potassium pyrogalloldisulphonate, $C_6H_4O_3(SO_3K)_2,2H_2O$; the *sodium* salt, with $3\frac{1}{2}H_2O$, and the *ammonium* salt, with $2H_2O$, are crystalline and readily soluble in water ; the *aluminium* and *magnesium* salts form small needles slightly yellow in colour.

J. J. S.

Action of Hydrobromic and Hydrochloric Acids on the so-called Dinaphthylene Glycol. By R. FOSSE (*Compt. rend.*, 1901, **133**, 236—237).—The compound obtained by the action of hydrobromic acid at 100° on the so-called dinaphthylene glycol can be obtained free from hydrogen bromide and water by crystallising it from hot glacial acetic acid, and it then has the composition $C_{21}H_{13}OBr$, melts at 218—220°, and is identical with bromodinaphthoxanthene. When boiled with alcohol, it yields dinaphthoxanthene, hydrogen bromide, and aldehyde. The product formed by the action of hydrochloric acid on the so-called glycol is identical with chlorodinaphthoxanthene and resembles the bromo-derivative in its properties. C. H. B.

Action of Benzoyl Chloride on Trioxymethylene in presence of Zinc Chlorine. By Marcel Descudé (*Compt. rend.*, 1901, **133**, 371—373).—The substance to which the formula $C_{14}H_{12}O_4$ was ascribed (this vol., i, 504) is *methylene dibenzoate*, $CH_2(OBz)_2$, and can also be obtained by the action of benzoic anhydride on trioxymethylene in presence of zinc chloride; it forms large, colourless, monoclinic crystals, melts at 99°, boils and slightly decomposes at 255°, and has a sp. gr. 1·275 at 22°. Its solubility in 100 parts of solvent at 24° is: absolute alcohol, 2·5; ether, 8; acetone, 18; and benzene, 27.

W. A. D.

Derivatives of Dialkylaminobenzoyltetrachlorobenzoic and Dialkylamino-*m*-hydroxybenzoyltetrachlorobenzoic Acids. Corresponding Dialkylaminoanthraquinones and Dialkylaminohydroxyanthraquinones. By Albin Haller and Herm. Umbgrove (*Bull. Soc. Chim.*, 1901, [iii], **25**, 745—749. Compare this vol., i, 469). —*Nitrosodimethylaminobenzoyltetrachlorobenzoic acid*,

$$NMe_2\cdot C_6H_3(NO)\cdot CO\cdot C_6Cl_4\cdot CO_2H,H_2O,$$

obtained by the action of nitrous acid on dimethylaminobenzoyltetrachlorobenzoic acid, crystallises in yellow scales melting at 129—130°; it loses its water of crystallisation at 110°, and then melts at 145°. *Nitrodimethylaminobenzoyltetrachlorobenzoic acid*, prepared by the action of fuming nitric acid on dimethylaminobenzoyltetrachlorobenzoic acid in acetic acid solution, crystallises in yellow scales melting at 147°.

Diethylamino-m-*hydroxybenzoyltetrachlorobenzoic acid*, obtained by the action of diethyl-*m*-aminophenol on tetrachlorophthalic anhydride, forms colourless crystals melting at 198°; when heated in sulphuric acid solution with dimethyl-*m*-aminophenol, it gives rise to *dimethyldiethyltetrachlororhodamine*, which forms violet-bronze crystals. *Diethylamino*-m-*hydroxybenzyltetrachlorobenzoic acid*, obtained by reducing the corresponding benzoyl derivative with zinc and hydrochloric acid, forms small, white crystals melting at 205°.

3-*Diethylamino*-5 : 6 : 7 : 8-*tetrachloroanthraquinone*, prepared by the condensation of diethylaminobenzyltetrachlorobenzoic acid by means of sulphuric acid, crystallises in dark red needles melting at 144°.

3-*Diethylamino*-1-*hydroxy*-5 : 6 : 7 : 8-*tetrachloroanthraquinone*, obtained in an analogous manner from the *m*-hydroxy-acid, crystallises in violet-bronze scales melting at 192°. N. L.

Esters of Anthranilic Acid. By Hans Mehner (*J. pr. Chem.*, 1901, [ii], **64**, 70—85. Compare this vol., i, 470).—The author shows that the solid substance obtained by Erdmann (this vol., i, 536) by the condensation of ethyl formate and methyl *o*-aminobenzoate in the presence of sodium is not ethyl *o*-aminobenzoylformate,

$$NH_2\cdot C_6H_4\cdot CO\cdot CO_2Et,$$

but *ethyl* o-*formylaminobenzoate*, $HCO\cdot NH\cdot C_6H_4\cdot CO_2Et$. It can also be prepared by heating formic acid with ethyl *o*-aminobenzoate at 125—130°. When heated with phosphoric oxide, it gives the odour of *iso*nitriles. It crystallises from petroleum in colourless needles or prisms, melts at 57° (Erdmann gives m. p. 49°), and does not form a hydrazone or acetyl derivative. When treated with sodium nitrite and hydrochloric acid, it slowly passes into solution with the formation of *o*-carbethoxybenzenediazonium chloride, $N_2Cl\cdot C_6H_4\cdot CO_2Et$, and elimination of the formyl group. With aniline, this diazonium salt gives *ethyl o-diazoaminobenzoate*, $N_3HPh\cdot C_6H_4\cdot CO_2Et$, which crystallises in yellow needles, melts at 76°, is also obtained from aniline and diazotised ethyl *o*-aminobenzoate, and when boiled with dilute alcohol yields 3-phenylphentriazone.

The oil which Erdmann obtained, together with the solid, contains no ethyl *o*-aminobenzoylformate, but consists mainly of methyl *o*-formylaminobenzoate, as on diazotising and treating with aniline, methyl *o*-diazoaminobenzoate (m. p. 71°) is formed. *Methyl o-formylaminobenzoate*, $HCO\cdot NH\cdot C_6H_4\cdot CO_2Me$, prepared by heating methyl *o*-aminobenzoate and formic acid at 130°, crystallises in aggregates of needles melting at 54°, and when heated with phosphoric oxide gives the odour of *iso*nitriles. The *formate* of methyl *o*-aminobenzoate is produced when the ester and formic acid are heated at 100°, and crystallises in white needles melting at 58°.

Ethyl o-acetylaminobenzoate, $NHAc\cdot C_6H_4\cdot CO_2Et$, prepared from ethyl *o*-aminobenzoate and acetic anhydride, crystallises in colourless needles or prisms melting at 64—65°; the *benzoyl* derivative crystallises in colourless needles melting at 98°.

Methyl o-benzoylaminobenzoate, $NHBz\cdot C_6H_4\cdot CO_2Me$, forms colourless needles melting at 100°. K. J. P. O.

Lobaric and Usnetic Acids. By OSWALD HESSE (*J. pr. Chem.*, 1901, [ii], **64**, 110—112. Compare this vol., i, 149).—The author demonstrates that Zopf's suggestion (Abstr., 1897, i, 436) that lobaric acid is merely impure usnetic acid is incorrect. Lobaric acid is a definite chemical substance. K. J. P. O.

Condensation of *iso*Butaldehyde with *p*-Hydroxy- and *p*-Ethoxy-benzaldehydes. By ARNOLD HILDESHEIMER (*Monatsh.*, 1901, **22**, 497—504).—No condensation occurs between *p*-hydroxybenzaldehyde and *iso*butaldehyde in alcoholic solution to which concentrated aqueous potassium carbonate has been added; when alcoholic potassium hydroxide is used, the *p*-hydroxybenzaldehyde is recovered unchanged, but the *iso*butaldehyde is converted into *iso*butyric acid and $\beta\beta\delta$-trimethyl-$\alpha\gamma$-pentanediol. In presence of aqueous potassium carbonate, *p*-ethoxybenzaldehyde and *iso*butaldehyde yield the *aldol*, $OEt\cdot C_6H_4\cdot CH(OH)\cdot CMe_2\cdot CHO$, which crystallises from alcohol on adding water, and melts at 66—67°; it does not yield an oxime or an acetate, but on reduction with sodium amalgam gives *α-p-ethoxyphenyl-$\beta\beta$-dimethyl-$\alpha\gamma$-propanediol*, $OEt\cdot C_6H_4\cdot CH(OH)\cdot CMe_2\cdot CH_2\cdot OH$, which melts at 75°, boils at 220—222° under 24 mm. pressure, and is also obtained, along with *iso*butyric acid, by the direct condensation of *p*-ethoxybenzaldehyde and *iso*butaldehyde in presence of alcoholic potassium hydroxide; the *diacetate*, $C_{17}H_{24}O_5$, of the glycol crystallises from alcohol in colourless, well-formed plates and melts at 70°.

W. A. D.

Electrolytic Reduction of *o*-Nitroanthraquinone in Alkaline, and of 1 : 5- and α-Dinitroanthraquinone in Acid Solution. By JOHANN MÖLLER (*Zeit. Elektrochem.*, 1901, 7, 797—800).—*o*-Nitroanthraquinone may be reduced to the corresponding amino-compound in slightly alkaline solution by the method of Elbs and Kopp (Abstr., 1899, i, 270). The product is purer than that obtained by the reduction in acid solution (this vol., i, 598).

1 : 5-Dinitroanthraquinone dissolved in glacial acetic acid containing some sulphuric acid is reduced at 100° by a current of 0·011 ampere per sq. cm. to diaminoanthraquinone. Platinum electrodes were used. The yield is small, the principal product being a compound which dissolves in aqueous sodium hydroxide to a blue solution.

α-Dinitroanthraquinone (m. p. 258—263°), reduced under the same conditions as the preceding, gave very similar results, the principal product being a colouring matter which dissolved in sodium hydroxide solution to a blue liquid. A small yield of α-diaminoanthraquinone was also obtained.

T. E.

Artificial Camphor and Camphene. By IWAN L. KONDAKOFF (*Chem. Zeit.*, 1901, 25, 609—610).—A discussion of the various views held as to the constitution of artificial camphor, and the relation between it and camphene hydriodide (Kondakoff and Lutschinin, this vol., i, 282).

R. H. P.

Apiin and Apiose. By EDUARD VONGERICHTEN (*Annalen*, 1901, 318, 121—136. Compare this vol., i, 40).—*Apiose*, a new pentose, obtained by hydrolysing apiin, $C_{26}H_{28}O_{14}$, with ½—1 per cent. sulphuric acid, is isolated in the form of a light yellow syrup. It is slightly dextrorotatory and fermentable, but these properties may be due to traces of dextrose. The *osazone* crystallises in yellow needles; its melting point is indefinite, the substance softening at 145° and melting at 155°. *Apiose*-p-*bromophenylosazone*, prepared from *p*-bromophenylhydrazine and the pentose, crystallises in rosettes of yellow needles and melts at 211—212°. These derivatives readily dissolve in alcohol, but are much less soluble in water. Apiose behaves quite unlike arabinose and rhamnose when treated with Tollens' phloroglucinol reagent (Abstr., 1892, 290); the latter pentoses yield red and yellow colorations respectively, whilst the new sugar gives a thick, brown, amorphous precipitate; it also differs from the ordinary pentoses in not furnishing furfuraldehyde on distillation with hydrochloric acid.

Apigenin or apiin, when hydrolysed with concentrated sodium hydroxide solution, yields *p*-hydroxyacetophenone, phloroglucinol, and carbon dioxide. The sugar residue of the apiin molecule does not appear to undergo hydrolysis under these conditions, for the alkaline solution, after neutralisation, does not react with Fehling's solution until it has been boiled with hydrochloric acid.

Apiin, when boiled for 5 hours with 25 per cent. sodium hydroxide solution, becomes hydrolysed into *p*-hydroxyacetophenone and *apiosedextrosephloroglucinol*, $C_{11}H_{19}O_9 \cdot O \cdot C_6H_3(OH)_2$; the latter product, obtained in the form of a reddish-brown syrup, gives a slight reduction with Fehling's solution, and is hydrolysed into phloroglucinol, apiose, and dextrose; these compounds, however, interact, yielding a brown, amorphous substance.

A dilute solution of apiosedextrosephloroglucinol, treated with benzenediazonium chloride in the presence of sodium carbonate, yields a red *azo*-compound which, when crystallised from alcohol, has the composition $C_{29}H_{32}O_{12}N_4$. This compound is insoluble in cold sodium carbonate solution, but dissolves on warming, and is reprecipitated on cooling or by the addition of a mineral acid. The solution obtained by boiling the azo-derivative with dilute sulphuric acid reduces Fehling's solution.

Apiin and apiosedextrosephloroglucinol are not hydrolysed by emulsin, yeast, or Fischer's yeast extract (Abstr., 1895, ii, 322). Dextroseapigenin, on the other hand, is readily decomposed by emulsin, yielding apigenin and dextrose.

Apiin is lævorotatory in alkaline solutions, a 6 per cent. solution containing 1 mol. of sodium hydroxide having a rotation of $-120°$; the further addition of alkali changes the colour of the solution from dark yellow to pale yellow, and increases the rotatory power by 1° to 1·5°.

G. T. M.

Acetyl Derivatives of Jalapin and Jalapic Acid. By Nicolai Kromer (*Arch. Pharm.*, 1901, **239**, 384—388).—*Pentacetyljalapin* (jalapin pentacetate), $C_{34}H_{58}O_{20}(C_5H_9O)_3Ac_5$, prepared by heating jalapin at 135° with acetic anhydride and sodium acetate, forms a yellow, amorphous powder resembling jalapin. *Decacetyljalapic acid*, $C_{34}H_{56}O_{20}Ac_{10}$, forms a pale yellow, amorphous mass.

K. J. P. O.

Nature and Origin of the Poison of Lotus Arabicus. By Wyndham R. Dunstan and Thomas A. Henry (*Proc. Roy. Soc.*, 1901, **68**, 374—378. Compare this vol., i, 39—40).—Lotusin has the formula $C_{28}H_{31}O_{16}N$ instead of $C_{22}H_{19}O_{10}N$, which was provisionally assigned to it. It is readily hydrolysed by dilute hydrochloric acid, with formation of dextrose (2 mols.), hydrogen cyanide (1 mol.), and lotoflavin (1 mol.). When warmed with aqueous alkalis, it is gradually decomposed with production of ammonia and lotusinic acid.

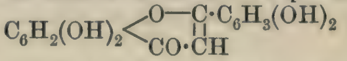
Lotusinic acid, $C_{28}H_{32}O_{18}$, is monobasic, and furnishes yellow, crystalline salts; it is readily hydrolysed by dilute acids with formation of lotoflavin, dextrose, and heptogluconic acid.

Lotoflavin is readily soluble in alcohol or hot glacial acetic acid; it yields a *tetracetyl* derivative, and two isomeric, mutually convertible, *trimethyl* ethers which furnish the same *acetyltrimethyllotoflavin*. By the action of fused potassium hydroxide, lotoflavin is converted into phloroglucinol and β-resorcylic acid.

Determination of the amount of hydrogen cyanide, yielded by *Lotus arabicus* at different stages of its growth has shown that the maximum of lotusin occurs in mature plants bearing seed-pods and flowers.

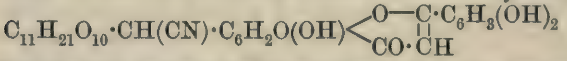
Lotase resembles emulsin, but has only a feeble effect on amygdalin, and is much more readily deprived of its hydrolytic power by the action of heat or alcohol.

The constitution of lotoflavin is represented by the formula



$$C_6H_2(OH)_2 < \begin{array}{l} O - C \cdot C_6H_3(OH)_2 \\ \quad\ \ \| \\ CO \cdot CH \end{array} \ [OH = 4:6:2':4'],$$

whilst lotusin is a lotoflavin ether of maltose-cyanohydrin,



$$C_{11}H_{21}O_{10} \cdot CH(CN) \cdot C_6H_2O(OH) < \begin{array}{l} O - C \cdot C_6H_3(OH)_2 \\ \quad\ \ \| \\ CO \cdot CH \end{array} \ [OH = 4:2':4'].$$

The position assigned to the cyanogen group is supported by the fact that mandelonitrile, lævulose cyanohydrin, and pentacetylgluconitrile are, like lotusin, easily decomposed by dilute hydrochloric acid with formation of hydrogen cyanide and the corresponding aldehyde or ketone. E. G.

Saponins and their Distribution. By Ludwig Weil (*Arch. Pharm.*, 1901, **239**, 363—373).—The amounts of saponin and saponic acid have been estimated in a number of plants. The ripe seeds of *Camellia theifera*, Griff, contain 0·5 per cent. theosaponic acid and 10 per cent. theosaponin, $C_{18}H_{28}O_{10}$, the roots and the twigs respectively 4 and 2·5 per cent. of this saponin. The dried seeds of *Aesculus Hippocastanum* yield 10 per cent. of the saponin $C_{16}H_{24}O_{10}$. From the soft parts of the dried berries of *Sapindus Mukorossi*, 10·5 per cent. of the saponin, $C_{17}H_{26}O_{10}$, is obtained. In the same part of the plant, *Acacia concinna* contains 5 per cent., and *A. concinna* var. *rugata* 4 per cent., of the saponin $C_{20}H_{32}O_{10}$, *Balanites Roxburghii* contains in the soft parts of the fruit 7 per cent. of the saponin $C_{18}H_{28}O_{10}$. *Illipe latifolia* contains 9·5 per cent. of the saponin $C_{17}H_{26}O_{10}$, in the dried cotyledons, and *Barringtonia Vriesei* 1 per cent. in the bark, and 8 per cent. in the seeds, of the saponin $C_{18}H_{28}O_{10}$.

These saponins are closely related to others already obtained from other plants, and are readily hydrolysed in dilute solution by 2 per cent. sulphuric acid to sapogenin and sugar. K. J. P. O.

Tannin contained in Sequoia Gigantea. By Georg Heyl (*Chem. Centr.*, 1901, ii, 312—313; from *Pharm. Centr.-H.*, **42**, 379—390).—The *tannin*, $C_{21}H_{20}O_{10}$, contained in the fir cones of *Sequoia gigantea*, is a pale reddish-brown powder, and is soluble in water, forming a solution which soon becomes turbid; it is soluble also in alkalis, ammonia, and alkali carbonates, forming reddish-brown solutions, and its alcoholic solution has a blood-red colour. It is insoluble in ether, chloroform, light petroleum, glacial acetic acid, or benzene, and gives a brownish-black precipitate with ferric chloride.

The *bromo*-derivative, $C_{21}H_{15}O_{10}Br_5$, the *acetyl* derivative, $C_{21}H_{14}O_{10}Ac_6$, and the *benzoyl* derivative, $C_{21}H_{14}O_{10}Bz_6$, are described. With salts of calcium, magnesium, barium, copper, or lead, the tannin gives precipitates which, when heated at 200°, yield pyrogallol, and when boiled with dilute sulphuric acid form mainly phlobaphene, together with some gallic acid and sugar. The *tannoform*, $CH_2(C_{21}H_{19}O_{10})_2$, is precipitated by formaldehyde from concentrated solutions of the tannin as a gelatinous mass, but separates from dilute solutions on adding hydrochloric acid in flesh coloured flakes; it is insoluble in almost all solvents.

E. W. W.

Pyromucic and *iso*Pyromucic Acids. By Chavanne (*Compt. rend.*, 1901, **133**, 167—169).—Pure *iso*pyromucic acid melts at 91°; 100 grams of water dissolve 4·5 grams of it, and only 2·7 grams of pyromucic acid at 0°. It dissolves unchanged in concentrated acids, but is decomposed by dilute alkalis. The *sodium* salt forms brilliant spangles, and gives an alkaline solution in water, which rapidly decomposes; the *potassium* salt is similar but extremely deliquescent; the *ammonium* salt loses ammonia in a vacuum. The *barium* salt, with $5H_2O$, and the *calcium* salt, with $3H_2O$, are sparingly soluble, crystalline powders; the *lead* salt contains $1H_2O$, and the *magnesium, zinc, cadmium, manganese, mercurous,* and *mercuric* salts are described. On mixing solutions of an alkali-salt of the acid and of copper sulphate, a red, crystalline, *cuprous* salt is formed; pyromucic acid, under similar conditions, gives the cupric salt with $3H_2O$.

*iso*Pyromucic acid is not esterified by alcohol and dry hydrogen chloride, although pyromucic acid readily yields its ethyl ester under these conditions. Its oxidation by bromine water and by potassium permanganate is similar to that of pyromucic acid; but in addition, it reduces Fehling's solution in the cold, and acid or alkaline solutions of silver; with phenylhydrazine, it yields a *compound*, $C_{11}H_{10}O_2N_2$, which crystallises in white needles, melts at 77°, gives the green coloration with ferric chloride characteristic of the parent acid, and is probably a *hydrazone* rather than a hydrazide, since its molecule requires for neutralisation the same quantity of alkali as the original acid. The phenylhydrazine derivative of pyromucic acid melts at 117°.

W. A. D.

Synthesis of Tropilidene. By Richard Willstätter (*Annalen*, 1901, **317**, 204—265. Compare this vol., i, 223).—The greater portion of the work discussed in this communication has already been published; the following data, however, are described for the first time.

The hydrogen chloride additive product of Δ^2-methyltropan yields an *aurichloride*, $C_9H_{17}N,HAuCl_4$, melting at 94—96°. The oily, basic dibromide of the same base furnishes a *platinichloride*,

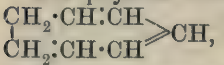
$$(C_9H_{17}NBr_2)_2,H_2PtCl_6,$$

crystallising in yellow needles and melting at 174—175°, and an *aurichloride* melting at 175—176°.

Ethyl Δ^2-cyclo*heptenecarboxylate*, $C_7H_{11}{\cdot}CO_2Et$, obtained by esterifying the acid with sulphuric acid and absolute alcohol, is a colourless oil having a fruity odour and boiling at 100° under 17 mm. pressure; it has a sp. gr. 0·9929 at 15°/4°. This ester is hydrolysed only with great difficulty, and when it is decomposed by a hot solution of potassium hydroxide in methyl alcohol, the original acid is not regenerated, but the Δ^1-isomeride is produced.

The *chloride*, $C_7H_{11}{\cdot}COCl$, of Δ^2-*cyclo*heptenecarboxylic acid is an oil boiling at 88—90° under 13 mm. pressure. The corresponding *hydrazide*, $C_7H_{11}{\cdot}CON_2H_3$, produced by heating the ethyl ester with hydrazine hydrate at 120°, crystallises from water or ethyl acetate in lustrous prisms melting at 137—139°, the *azide*, obtained from the hydrazide by the action of nitrous acid, is a colourless, explosive oil.

Tropilen, when reduced with zinc dust and acetic acid, yields a *ketone*, $C_7H_{12}O$, boiling at 169—170° (corr.); this substance, which gives a *semicarbazone* melting at 185—186°, is stable towards permanganate solution, and resembles the methyl*cyclo*hexanones.

The physical constants of the synthetical $\Delta^{1:3:5}$-*cyclo*heptatriene,  $\begin{matrix}CH_2\cdot CH{:}CH\\ CH_2{:}CH\cdot CH\end{matrix}{>}CH$, are tabulated and compared with those of other hydrocarbons having seven-membered rings. G. T. M.

Synthesis of Monocyclic Tropine Bases. By RICHARD WILLSTÄTTER (*Annalen*, 1901, 267—307. Compare this vol., i, 225 and preceding abstract).—The greater portion of the experimental part of this communication has already been published. The following compounds, however, are described for the first time.

*Methylamino*cyclo*heptadiene*, $C_7H_9\cdot NHMe$, obtained by treating tropilidene monohydrobromide with a benzene solution of methylamine, boils at 65—66° under 11 mm. and at 82° under 21·5 mm. pressure, it is somewhat soluble in cold water, but separates out when the solution is warmed. It readily absorbs carbon dioxide, forming a syrupy carbamate and yields an oily nitrosoamine. The *platinichloride*,

$$(C_8H_{13}N)_2,H_2PtCl_6,$$

crystallises from water in orange-red prisms and melts at 154—155°; the *aurichloride*, when first precipitated, is oily, but rapidly solidifies to form orange-yellow needles melting at 85°. The *benzoyl* compound, C_7H_9NMeBz, crystallises from light petroleum in rectangular plates and melts at 65—67°. The *phenylthiocarbamide*, $C_8H_{12}N\cdot CS\cdot C_6H_6N$, prepared by mixing its generators in ethereal solution, crystallises from alcohol either in white prisms, needles, or leaflets melting at 117—118°, or in colourless, four-sided plates melting at 125—126°. These forms, when crystallised separately, again yield crops containing both modifications. The remainder of the paper consists of a description of the preparation and properties of the Δ^2-, Δ^3- and Δ^4-methyltropans (dimethylamino*cyclo*heptenes) and their salts, the results being exhibited in tabular form. G. T. M.

Synthesis of Tropan and Tropidine. By RICHARD WILLSTÄTTER (*Annalen*, 1901, **317**, 307—374. Compare this vol., i, 225, and preceding abstract).—The outline of these syntheses has been given in a previous communication.

The *platinichloride*, $(C_9H_{18}NCl)_2,H_2PtCl_6$, obtained from the additive product of Δ^4-methyltropan and hydrogen chloride, crystallises from water either in prisms or four-sided plates and melts at 168°.

Tropan methiodide, $C_7H_{12}NMe_2I$, formed by treating the corresponding chloride with a concentrated solution of potassium iodide, crystallises from water in hopper-shaped aggregates and does not melt below 300°. Tropan methochloride, when heated above 300°, decomposes into tropan and methyl chloride.

The *platinichloride*, $(C_9H_{18}NCl)_2H_2PtCl_6$, prepared from the additive product of Δ^3-methyltropan and hydrogen chloride, crystallises from water either in hexagonal plates or in sphenoidal forms, and melts at 178°; the *aurichloride*, when crystallised in long needles, melts at 65—66°, but the melting point of different preparations is somewhat variable and indicates the existence of *cis*- and *trans*-modifications. The oily hydrogen chloride additive product itself is a mixture, for when dissolved in ether a portion undergoes rearrangement, yielding tropan methochloride, whilst the unchanged oil is stable even at 100°, furnishes a *platinichloride* melting at 183°, and is probably a derivative of the stable *cis-trans*-base.

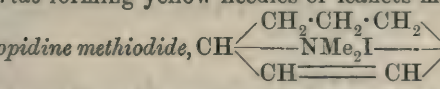
Merling's partial synthesis of tropidine from α-methyltropidine leads to the production of a mixture of *iso*tropidine and tropidine derivatives, in which the former predominate; the pure base has, however, been obtained from Δ^4-methyltropan.

2-*Bromotropan methiodide*, formed by treating the corresponding methobromide with a concentrated solution of potassium iodide, crystallises in prisms; it melts and decomposes at 262°.

Δ^3-Methyltropan forms a *dibromide* which changes into 6-*bromotropan methobromide*, a substance crystallising in acicular prisms and melting above 300°. The *platinichloride* of 6-bromotropan methochloride crystallises in hexagonal plates and melts at 250°. This bromotropan methobromide, when treated with alkalis, loses hydrogen bromide, yielding an unsaturated methobromide, which, when converted into the corresponding methochloride, furnishes a *platinichloride*,

$$(C_6H_{13}NMe)_2PtCl_6,$$

crystallising in orange, acicular prisms melting at 233—234°, and an *aurichloride* forming yellow needles or leaflets melting at 258°.

iso*Tropidine methiodide*,  $CH\left\langle\begin{array}{c}CH_2\cdot CH_2\cdot CH_2\\ NMe_2I\\ CH=\!=CH\end{array}\right\rangle CH$, produced by mixing *cyclo*heptadiene dibromide with a concentrated solution of methylamine in methyl alcohol or benzene and treating the tertiary base with methyl iodide, crystallises in four-sided plates and melts at 293°. From it, the methochloride is obtained which yields a *platinichloride*, $(C_9H_{13}NMe)_2PtCl_6$, crystallising in monoclinic prisms melting at 234—235°; and an *aurichloride* forming acicular prisms melting at 255—257°.

G. T. M.

Action of Pyridine Bases on Tetrahalogenated Benzoquinones. By HENRI IMBERT (*Compt. rend.*, 1901, **133**, 162—164).—Pyridine combines with chloroanil in boiling ethyl acetate solution containing a small quantity of acetic acid to form a red *compound*, $OH\cdot C_5NH_2\dot{:}C_6Cl_2O_2$ or $C_5NH_4\cdot C_6Cl_2O_2\cdot OH$, which is soluble in dilute alkalis, except ammonia, and also in acids; boiling alkalis remove chlorine, but boiling hydrochloric acid merely dissolves the compound. Neither quinoline nor 2-methylpyridine combines with chloroanil either in ethyl acetate or acetic acid solution, but 3-methylpyridine yields a *compound*, $C_5NH_3Me\cdot C_6Cl_2O_2\cdot OH$ or

$$OH\cdot C_5NHMe\dot{:}C_6Cl_2O_2,$$

which forms a brownish-red mass of microscopic needles.

Bromoanil yields with pyridine a compound similar to that obtained from chloroanil.

W. A. D.

Action of Pyridine Bases on Tetrahalogen Derivatives of Quinone. By HENRI IMBERT (*Compt. rend.*, 1901, 133, 233—236. Compare preceding abstract).—When the pyridyldichlorohydroxyquinone formed by the action of pyridine on tetrachloroquinone is boiled with alcoholic or aqueous potash it yields a compound, $OH\cdot C_5NH_2{:}C_6ClO_2\cdot OK$, or, more probably $C_5NH_4\cdot C_6ClO_2(OK)\cdot OH$, the compound $C_5NH_4\cdot C_6Cl_2O_2\cdot OK$ being formed as an intermediate product. The final product forms orange-red crystals soluble in water, and when treated with sulphuric acid yields *pyridylchlorodihydroxyquinone*, $C_5NH_4\cdot C_6ClO_2(OH)_2$, which crystallises in orange-red, microscopic needles soluble in hot alcohol, and in acids. It differs from pyridyldichlorohydroxyquinone in being generally more soluble, and producing a wine-red solution with alkalis. It is readily reduced by zinc and sulphuric acid, but not by sulphurous acid. The sodium salt is very soluble; the silver salt is brown and insoluble, and from it the *ethyl* and *benzoyl* salts can be obtained. They are both red, crystalline compounds. C. H. B.

Carbazole. By WILHELM VAUBEL (*Zeit. angew. Chem.*, 1901, 14, 784—785).—A solution of carbazole in glacial acetic acid, when treated with nascent bromine from hydrochloric acid, and potassium bromide and bromate, decolorises 2 mols. of bromine but forms a monobromide (m. p. 197·5°), which is probably identical with the 3-bromocarbazole obtained by Ciamician and Silber (Abstr., 1882, 1104). By the continued action of bromine, an impure *dibromide* melting at 170·5° was obtained. Carbazole may be titrated with bromine in glacial acetic acid solution, 2 mols. of bromine corresponding with 1 mol. of carbazole. R. H. P.

[Condensation Products of] Formaldehyde. By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1901, 25, 564).—Pentamethylenediamine condenses with a 40 per cent. solution of formaldehyde, precipitating a white *compound*, which is soluble in acids, but insoluble in alkalis, and decomposes when kept. A similar unstable, yellow *base* is obtained from *p*-phenylenediamine. *p*-Aminoacetanilide and formaldehyde condense in the presence of hydrochloric acid forming the *base*, $(NHAc\cdot C_6H_4\cdot NH\cdot CH_2)_2O$, which is obtained as a white, crystalline powder. The analogous *compound* from *p*-aminophenol is an unstable, reddish, amorphous powder. R. H. P.

Carbohydrazides of the Dihydroxybenzenes. By ALFRED EINHORN and RICHARD ESCALES (*Annalen*, 1901, 317, 190—203. Compare Abstr., 1898, i, 409).—Ketones of the type $X\cdot COMe$, where X is an aromatic radicle, condense with the carbohydrazides of the dihydroxybenzenes, yielding condensation products of the type $OH\cdot C_6H_4\cdot O\cdot CO\cdot NH\cdot N{:}CMeX$, but, under similar conditions, this reaction does not take place with ketones such as acetone, diethyl ketone, ethyl acetoacetate, phenyl ethyl ketone, benzophenone, and the saturated cyclic ketones.

Acetophenone catecholcarbohydrazone, $OH\cdot C_6H_4\cdot O\cdot CO\cdot NH\cdot N{:}CMePh$, produced, together with dicatecholcarbohydrazide,

$$N_2H_2(CO\cdot O\cdot C_6H_4\cdot OH)_2,$$

and *bis*phenylmethylazimethylene (Curtius and Than, Abstr., 1891, 1355) by condensing catecholcarbohydrazide and acetophenone in the presence of glacial acetic acid or zinc chloride, crystallises from alcohol in nacreous leaflets and melts at 190—191°; it is soluble in solutions of the caustic alkalis, and is resolved into its generators on boiling with concentrated hydrochloric acid. The *compound*

$OH\cdot C_6H_4\cdot O\cdot CO\cdot NH\cdot N\colon CMe\cdot C_6H_4Me$,

obtained from catecholcarbohydrazide and *p*-tolyl methyl ketone, crystallises in silky leaflets and melts at 185—186°.

Resorcinolcarbohydrazide, prepared by adding dry, powdered resorcinol carbonate to a cold solution of hydrazine hydrate in absolute alcohol and completing the action on the water-bath, crystallises from this solvent in white needles and melts at 160°.

Acetaldehyde resorcinolcarbohydrazone,

$OH\cdot C_6H_4\cdot O\cdot CO\cdot NH\cdot N\colon CHMe$,

obtained by treating the preceding compound with acetaldehyde, crystallises from water and melts at 150°; it is readily soluble in alcohol or acetone. The *benzaldehyde* compound, $OH\cdot C_6H_4\cdot O\cdot CO\cdot NH\cdot N\colon CHPh$, melts at 175°, and the *o-hydroxybenzaldehyde* compound,

$OH\cdot C_6H_4\cdot O\cdot CO\cdot NH\cdot N\colon CH\cdot C_6H_4\cdot OH$,

at 185—186°; the latter substance develops a greenish-black coloration with ferric chloride. The acetophenone derivative,

$OH\cdot C_6H_4\cdot O\cdot CO\cdot NH\cdot N\colon CMePh$,

produced by mixing its generators in warm, alcoholic solution in the presence of glacial acetic acid, melts at 174°. The *compound* $OH\cdot C_6H_4\cdot O\cdot CO\cdot NH\cdot N\colon CMe\cdot C_6H_4Me$, derived from resorcinolcarbohydrazide and *p*-tolyl methyl ketone, melts at 182°.

Resorcinol carbonate, when treated with diethylamine, yields a mixture of two substances, *resorcinolcarbodiethylamide*,

$OH\cdot C_6H_4\cdot O\cdot CO\cdot NEt_2$,

melting at 68—69°, and *resorcinoldicarbodiethylamide*, $C_6H_4(O\cdot CO\cdot NEt)_2$, boiling at 270° under 36·5 mm. pressure and melting at 35—36°; these compounds are separated by the action of sodium hydroxide, in which the former alone is soluble.

Acetaldehyde quinolcarbohydrazone, $OH\cdot C_6H_4\cdot O\cdot CO\cdot NH\cdot N\colon CHMe$, produced from acetaldehyde and quinolcarbohydrazide, separates from water in white crusts and melts at 177°. The corresponding *benzaldehyde* compound crystallises in nacreous leaflets and melts at 215°; the *o-hydroxybenzaldehyde* compound is obtained in needles softening at 180° and melting at 194°; the *acetophenone* derivative,

$OH\cdot C_6H_4\cdot O\cdot CO\cdot NH\cdot N\colon CMePh$,

forms needles melting at 120—121°, and its p-*tolyl* homologue melts at 208—209°.

G. T. M.

[Pyrazolone Derivatives from] Methyl α-Butyrylacetoacetate. By A. Bongert (*Compt. rend.*, 1901, 133, 165—167).—Whereas hydrazine acetate converts methyl α-butyrylacetoacetate (this vol., i, 311 and 500) into *methyl 5-methyl 3-propylpyrazole-4-carboxylate*, hydrazine hydrate gives rise initially to acetylhydrazide and methyl butyrylacetate, the latter then condensing with a second mol. of hydrazine to form 3-*propyl*-5-*pyrazolone*, which separates in white crystals and melts and sublimes at 196°.

The sodium derivative of methyl α-butyrylacetoacetate forms white crystals, melts at 142°, is not decomposed by cold water, and does not interact with methyl iodide. On adding methyl iodide, however, to a mixture of methyl α-butyrylacetoacetate and sodium methoxide, methyl acetate and *methyl methylbutyrylacetate*, $COPr^{\alpha}\cdot CHMe\cdot CO_2Me$, are formed. The latter boils at 86° under 16 mm. pressure. It combines with phenylhydrazine to form 1-*phenyl*-4-*methyl*-3-*propyl*-5-*pyrazolone*, which boils at 200° under 14 mm. pressure and separates from ether in white crystals melting at 78°. Hydrazine hydrate converts it into 4-*methyl*-3-*propyl*-5-*pyrazolone*, which forms white needles and melts at 189°.

Cold concentrated sulphuric acid hydrolyses methyl α-butyrylacetoacetate to butyric acid and methyl acetoacetate. W. A. D.

Nitroquinolones and Nitrocarbostyrils. By Herman Decker (*J. pr. Chem.*, 1901, [ii], **64**, 85—101).—In the literature, seven nitrocarbostyrils are described in which the nitro-group is in the benzene nucleus, whilst only four such compounds are theoretically possible. The author has reinvestigated these compounds, and studied the nitration of the 1-alkyl-2-quinolones and nitro-1-alkyl-2-quinolones.

6-*Nitro*-1-*methyl*-2-*quinolone*, $C_{10}H_8O_3N_2$, prepared by oxidising 6-nitroquinoline methiodide, crystallises in pale yellow needles melting at 222°. The corresponding *ethyl* derivative forms pale yellow needles melting at 183°.

7-Nitro-1-methyl-2-quinolone, prepared by oxidising 7-nitroquinoline methiodide or methyl sulphate, crystallises in yellow needles melting at 198—199°. 7-*Nitroquinoline ethiodide* forms large, ruby-red needles; 7-*nitro*-1-*ethyl*-2-*quinolone*, lustrous needles melting at 168—169°.

[With N. Kasatkin.]—The so-called [γ-] nitrocarbostyril (Friedländer and Lazarus, Abstr., 1885, 1138) is 6-nitrocarbostyril (6-nitro-2-hydroxyquinoline), as the sodium derivative yields 6-nitro-1-methyl-2-quinolone (m. p. 222°) with methyl iodide. The nitrobromocarbostyril (Abstr., 1892, 630) is then 3-bromo-6-nitro-2-hydroxyquinoline.

[With G. Pollitz.]—[ε-] Nitrocarbostyril (m. p. 302°) yields on alkylation 5-nitro-1-methyl-2-quinolone (m. p. 135°) and 5-nitro-1-ethyl-2-quinolone (m. p. 166°) respectively, and is therefore 5-nitrocarbostyril (compare Claus and Setzer, Abstr., 1896, i, 498). [ε-] Nitro-2-bromoquinoline, from which the nitrocarbostyril is obtained by the action of concentrated hydrochloric acid, has also the nitro-group in position 5.

[δ-] Nitrocarbostyril (m. p. 163°; Miller and Kinkelin, Abstr., 1889, 990), which is prepared in a similar manner from [δ-] nitro-2-bromoquinoline, is 8-nitrocarbostyril, as it yields on alkylation, nitro-alkyl-2-quinolones isomeric with the preceding. 8-*Nitro*-1-*methyl*-2-*quinolone*, prepared by boiling [δ-] nitrocarbostyril with methyl sulphate and concentrated sodium hydroxide, crystallises in long needles melting at 124—125°; the corresponding *ethyl* derivative forms needles or plates melting at 92°. 2-Bromoquinoline, on nitration, yields therefore in the normal manner 5- and 8-nitro-2-bromoquinolines.

[ζ-] Nitro-2-bromoquinoline (m. p. 244°; Claus and Pollitz, Abstr., 1890, 521) is not homogeneous, as it yields a mixture of 5- and 8-nitro-1-methyl-2-quinolones. [ζ-] Nitrocarbostyril (m. p. 283°) is therefore a mixture of 5- and 8-nitrocarbostyril.

Quinoline methyl sulphate yields on nitration only 5-nitromethylquinoline (compare Abstr., 1900, i, 689).

1-Methyl-2-quinolone yields on nitration with nitric acid (sp. gr. 1·4) only the 5-nitro-derivative, but with fuming nitric acid a mixture of mono-, di-, and tri-nitro-derivatives. *Trinitro*-1-*methyl*-2-*quinolone*, $C_9NH_3OMe(NO_2)_3$, crystallises in lustrous, pale yellow, insoluble needles, melting at 208—210°. 1-Ethyl-2-quinolone behaves in a similar manner. *Trinitro*-1-*ethyl*-2-*quinolone* forms dark yellow crystals melting at 224°. The nitration of the 1-alkylquinolones and of carbostyril is far more easily effected than that of quinoline.

Trinitro-1-*methyl*-2-*quinolone*, $C_9NH_3OMe(NO_2)_3$, prepared by nitration of 7-nitro-1-methyl-2-quinolone, forms large, orange-yellow crystals melting and decomposing at 249°. *Trinitro*-1-*ethyl*-2-*quinolone*, prepared similarly from 7-nitro-1-ethyl-2-quinolone, forms plates melting and decomposing at 237°.

7-*Nitrocarbostyril* is prepared from 7-nitroquinoline, which is treated with hypochlorous acid, and the additive product decomposed by sodium hydroxide; it crystallises in lustrous, pale-yellow, insoluble needles, melting at 340°.

Of [α-] and [β-] nitrocarbostyril (Friedländer and Lazarus, *loc. cit.*), the author believes that the former is identical with 7-nitrocarbostyril, whilst the latter is either very impure 6-nitrocarbostyril or the nitro-group is in the pyridine nucleus. K. J. P. O.

Hydrochloride of Phenylhydrazine Ureide [Diphenylcarbazide]. By Paul Cazeneuve (*Bull. Soc. Chim.*, 1901, [iii], **25**, 757—758. Compare this vol., i, 292).—*Diphenylcarbazide hydrochloride*, $C_{13}H_{14}ON_4,HCl$, is prepared by adding a large excess of a saturated ethereal solution of hydrogen chloride to an alcoholic solution of diphenylcarbazide; it forms cauliflower-like masses of small white crystals, melting and decomposing at 125°. N. L.

Violet Chromium Colouring Matters derived from Diphenylcarbazide. By Paul Cazeneuve (*Bull. Soc. Chim.*, 1901, [iii], **25**, 758—761).—The violet colouring matter (Abstr., 1900, ii, 627) formed by the action of diphenylcarbazide on chromic acid has been obtained in the form of a violet-black, amorphous powder, the composition of which varies with the conditions of its preparation; its tinctorial properties are of no practical interest. A similar compound is formed by dimethyldiphenylcarbazide, but not by diphenylcarbazone. N. L.

α-Azoxynaphthalene. By Leonhard Wacker (*Annalen*, 1901, **317**, 375—385).—The amorphous compound obtained by Jaworsky (*J. pr. Chem.*, 1865, **94**, 283) on reducing α-nitronaphthalene with sodium amalgam in alcoholic solution is also produced by reducing the nitro-compound with zinc dust and alcoholic potassium hydroxide solution. It does not seem to have the properties of an azoxy-compound, and does not yield α-azonaphthalene on reduction.

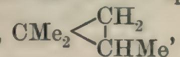
A crystalline *α-azoxynaphthalene* is prepared together with α-naphthylhydroxylamine, by reducing α-nitronaphthalene with zinc dust in dilute alcoholic solution containing ammonium chloride; it is also formed, together with α-naphthylamine, when α-naphthylhydroxylamine is heated on the water-bath.

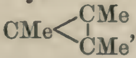
It slowly separates from acetone or light petroleum in thick, red prisms, and from alcohol in yellow, or reddish-brown, rhombic crystals; the former modification melts at 126·5° and the latter at 127°, both forms have the same chemical properties, and belong to the rhombic system. A solution of the substance in concentrated sulphuric acid is reddish-violet, slowly changing into blue; when warmed with more dilute acid (65 per cent. H_2SO_4), the α-azoxynaphthalene dissolves, yielding a blue solution, from which water precipitates a compound, soluble in aqueous sodium hydroxide to a red solution. These changes indicate a transformation of the azoxy-compound into a hydroxyazo-derivative. Filter paper soaked in the dilute, yellow, alcoholic solution of the azoxy-compound, soon becomes red when exposed to sunlight; a similar phenomenon is noticed in the case of azoxybenzene. α-Azonaphthalene is produced by the reduction of the new azoxy-derivative with zinc dust in an alcoholic solution of potassium hydroxide. G. T. M.

Decomposition Products of Edestin. By P. A. LEVENE and LAFAYETTE B. MENDEL (*Amer. J. Physiol.*, 1901, 6, 48—52).—The crystallised vegetable proteid edestin resembles the ordinary animal proteids in yielding the three known hexon bases, and so differs from the vegetable proteids, which are soluble in alcohol, and yield no lysine.
W. D. H.

Action of Reducing Agents on Hæmatin. By J. A. MILROY (*Proc. Physiol. Soc.*, 1901, xiv—xvi).—Hæmin was prepared by crystallisation from acetone containing hydrochloric acid: hæmatin was prepared from this, dissolved in glacial acetic acid and reduced by aluminium powder. After 24 hours, a bright red reduction product is formed which gives spectroscopic bands similar to those of oxyhæmoglobin, with the addition of a faint band in the red. This substance is soluble in chloroform and in ammonia; in ammonia, it shows no change in the absorption bands. It contains only a trace of iron, possibly due to the adherence of some unchanged hæmatin. After re-solution in glacial acetic acid and further reduction with zinc dust between 50° and 60°, the solution becomes green, and shows two absorption bands, one on each side of the D line; in this, it resembles the bilicyanin of Heynsius and Campbell. In chloroform, it becomes greenish-blue with a red fluorescence. It is soluble in dilute alkalis, but readily undergoes changes on exposure to air. The examination of these substances is not yet completed. W. D. H.

Organic Chemistry.

Trimethyltrimethylenes. By NICOLAI D. ZELINSKY and J. ZELIKOFF (*Ber.*, 1901, **34**, 2856—2867).—When diacetonealcohol is reduced with sodium amalgam, it forms *trimethyltrimethylene glycol*, $OH\cdot CMe_2\cdot CH_2\cdot CHMe\cdot OH$, which is a sweet, viscous liquid boiling at 135—136° under 40 mm. pressure, has a sp. gr. 0·9254 at 17°/4°, and a refraction $n = 1·4311$ at 17°, and when treated with hydrogen bromide yields the *dibromide*, $CMe_2Br\cdot CH_2\cdot CHMeBr$, which boils at 82° under 21 mm. pressure and has a sp. gr. 1·5316 at 20°/4°. 1 : 1 : 2-*Trimethyltrimethylene*,  $CMe_2<\begin{matrix}CH_2\\|\\CHMe\end{matrix}$, obtained by reducing the dibromide with zinc dust, boils at 56—57° under 750 mm. pressure, has a sp. gr. 0·6822 at 19·5°/4°, a refraction $n_D = 1·3848$ at 19·5°, decolorises permanganate very slowly, and is distinct from the hexylene described by Couturier (Abstr., 1893, i, 245), whose work has been repeated and confirmed by the present authors.

Methylacetylacetone, when reduced with sodium amalgam, yields a mixture of the *ketonealcohol*, $CHMeAc\cdot CHMe\cdot OH$, which boils at 104—107° under 20 mm. pressure, has a sp. gr. 0·9937 at 18°/4°, and a refraction $n_D = 1·4512$ at 18°, and the *trimethyltrimethylene glycol*, $OH\cdot CHMe\cdot CHMe\cdot CHMe\cdot OH$, which boils at 113—116° under 20 mm. pressure, has a sp. gr. 0·9906 at 14°/4°, and a refraction $n_D = 1·4524$ at 14°. The glycol, when treated with hydrogen bromide, forms a *dibromide* which boils at 95—100° under 30 mm. pressure, and when reduced with zinc dust yields 1 : 2 : 3-trimethyltrimethylene. 1 : 2 : 3-*Trimethyltrimethylene*,  $CMe<\begin{matrix}CMe\\|\\CMe\end{matrix}$, boils at 65—66° under 748 mm. pressure, has a sp. gr. 0·6921 at 22°/4°, and a refraction $n_D = 1·3942$ at 22°. The *diiodide* corresponding with the dibromide, when reduced with zinc dust, yields the γ-methylpentane described by Wislicenus (Abstr., 1883, 967), whose work has been repeated and confirmed by the present authors.

R. H. P.

The so-called Iodoacetylene. By ALBERTO PERATONER and R. SPALLINO (*Ber.*, 1901, **34**, 2718—2722).—The non-poisonous iodoacetylene described by Paternò and Peratoner (Abstr., 1890, 1219) can only be obtained from the impure acetylene prepared by the action of hydrochloric acid on copper acetylide, and is shown to be a mixture of solid diiodoacetylene, acetylene, vinyl chloride, and ethylidene dichloride. The only known iodo-derivative of acetylene is therefore the poisonous and malodorous compound prepared by Baeyer (Abstr., 1885, 1199) and shown by Nef (Abstr., 1889, i, 104) to be a diiodoacetylene.

T. M. L.

The Rendering Active of Oxygen. VII. By CARL ENGLER and WILHELM FRANKENSTEIN (*Ber.*, 1901, **34**, 2933—2941. Compare Abstr., 1897, ii, 402; 1899, i, 189, 221; 1900, i, 399).—A considerable precipitate of a *diperoxide*, $C_8H_{10}O_4$, is produced when a 5—7 per cent. benzene solution of dimethylfulvene [*iso*propylidene*cyclo*pentene] (Thiele, Abstr., 1900, i, 299) is stirred automatically in contact with the air or is shaken automatically in a bottle the air in which is repeatedly renewed. The oxidation is complete after 4—6 days. The same product is formed, only more slowly, when air or oxygen is passed through the solution without stirring. Light and a rise in temperature are two important factors which accelerate the precipitation; when, however, the temperature is too high, secondary reactions occur, and the original insoluble oxidation product becomes converted into substances soluble in benzene. Dimethylfulvene diperoxide forms a colourless powder, which explodes at 130°, and also when warmed with concentrated sulphuric acid. It is insoluble in most organic solvents, but dissolves in nitrobenzene, acetic acid, or alkalis, but at the same time is decomposed. It does not give the usual test for peroxides, namely, a yellow coloration with titanic acid, unless ether, alcohol, ethyl acetate, or chloroform is present.

Methylethylfulvene [*β-butylidene*cyclo*pentene*] is an orange-coloured liquid boiling at 185° under atmospheric pressure, and also yields a peroxide. Methylphenylfulvene also absorbs oxygen, but less readily than the simple alkyl fulvenes; the *diperoxide*, $C_{13}H_{12}O_4$, can be precipitated from the benzene solution by the aid of ether, but when once precipitated will not dissolve in benzene.

*cyclo*Pentadiene also absorbs oxygen, but so far no definite product has been isolated. The oxidation of hexylene and of dimethylfulvene has been studied by the aid of *N*/25 sodium indigotindisulphonate as described in the case of pentane. The numbers in the case of hexylene point to the direct addition of 1 mol. of oxygen, and the subsequent transference of one atom to the indigo. J. J. S.

Basic Properties of Oxygen. By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1901, **34**, 2679—2698).—All classes of organic oxygen compounds form salt-like derivatives with complex acids, whilst in a few cases similar compounds are formed with simple acids, the salts of dimethylpyrone, described by Collie and Tickle (Trans., 1899, **75**, 710), being of this class. Each basic oxygen atom is capable of combining with an amount of acid equivalent to one hydrogen ion, normal and acid salts being formed with polybasic acids. The constitution of these compounds cannot be expressed in terms of the ordinary formulæ, in which oxygen is bivalent, but may be expressed by supposing either that the oxygen in these compounds is quadrivalent (oxonium theory of Collie and Tickle), or that these salts are complex compounds (Werner), oxygen possessing one complex and two ordinary valencies. Which of the two theories is the more applicable to the facts has not yet been decided. The introduction of positive groups into an oxygen compound appears to increase the basicity, as it does in the case of ammonia, whilst negative groups diminish it, and it also appears to be the case that the less stable the form of combination of the oxygen, the greater the tendency to form salts. The following salts, representative of the various classes of organic oxygen compounds, have been prepared.

1. *Ethers.*—Ethyl ether, when added to an acid solution of potassium ferrocyanide, produces a crystalline precipitate of a *compound* of ethyl ether with ferrocyanic acid, which, however, rapidly decomposes and changes in appearance.

Ferricyanic and cobalticyanic acids behave in a similar manner. Di*iso*amyl ether combines with ferricyanic acid, and unites with cobalticyanic acid to form a *compound*, $C_{10}H_{22}O,H_3Co(CN)_6,2H_2O$, which crystallises like ammonium chloride and is decomposed by water. Anisole with ferricyanic acid yields six-sided tablets, and phenetole gives a solid film; paraldehyde with ferrocyanic acid gives large, rhombic plates.

2. *Ethylene Oxide and allied Substances.*—Ethylene oxide forms a crystalline compound at a low temperature with ferrocyanic acid. Cineol forms crystalline salts with simple acids, the hydrochloride and hydrobromide having been already described by Wallach (*Annalen*, 1884, **225**, 297; 1888, **246**, 280). The *phosphate* is a gelatinous mass; the *hydroferrocyanide*, $2C_{10}H_{18}O,H_4Fe(CN)_6,\frac{1}{2}H_2O$, is a white powder; the *hydroferricyanide* has the composition $2C_{10}H_{18}O,H_3Fe(CN)_6,3H_2O$, and unites with 1 mol. of acetone. The *hydrocobalticyanide* crystallises in colourless needles and may be used for the preparation of pure cobalticyanic acid. Pinol yields a crystalline *compound* with ferricyanic acid, and an amorphous one with ferrocyanic acid.

3. *Alcohols.*—The *compound* of amyl alcohol and ferricyanic acid crystallises in needles. Borneol unites with all three acids. The *hydrocobalticyanide* has the composition $2C_{10}H_{18}O,H_3Co(CN)_6$. Menthol and tetrahydrocarveol give with ferricyanic acid indistinctly crystalline powders. Trimethylcarbinol and amylene hydrate unite with ferrocyanic acid, whilst *iso*butyl alcohol does not.

4. *Acids.*—The only compound of this class appears to be the perbromide of the hydrobromide of acetic acid (Steiner, this Journ., 1874, 566).

5. *Esters.*—Ferricyanic acid unites with ethyl acetate, yielding flat prisms; with ethyl benzoate, forming orange-coloured needles; with ethyl oxalate, giving rhombic tablets; and with *iso*amyl valerate, yielding an indistinctly crystalline powder. With ferrocyanic acid, ethyl oxalate readily yields large, rhombic tablets of the formula $C_6H_{10}O_4,H_4Fe(CN)_6$.

6. *Aldehydes.*—Heptaldehyde does not unite with ferrocyanic acid, but forms a crystalline powder with ferricyanic acid. Benzaldehyde gives an amorphous compound with ferrocyanic acid, orange-coloured needles with ferricyanic acid, and thin prisms with cobalticyanic acid. Cinnamaldehyde has long been known to form a nitrate (Dumas and Peligot, *Annalen*, 1835, **14**, 65). It also forms, with ferrocyanic acid, rhombic tablets, with ferricyanic acid a crystalline powder, and with chloroplatinic acid orange-red prisms of the *platinichloride*.

7. *Ketones.*—Diethyl ketone yields rhombic plates with ferrocyanic acid, and a crystalline powder with ferricyanic acid. Dipropyl ketone gives irregular plates with ferrocyanic acid, and an oil with ferricyanic acid. Acetophenone gives rhombic plates with ferrocyanic acid, and an amorphous compound with ferricyanic acid. 1:3-Methyl*cyclo*hexanone yields a crystalline powder with ferrocyanic acid and small needles with ferricyanic acid. Menthone forms an indistinctly crys-

talline powder with ferrocyanic acid and small needles with ferricyanic acid. Tetrahydrocarvone gives long needles with ferrocyanic acid and a crystalline powder with ferricyanic acid. Suberone yields small prisms with ferrocyanic acid, and small needles with ferricyanic acid. *p*-Diketohexamethylene unites with phosphotungstic acid to form a *compound* which crystallises from water in well-developed, long tablets. Several compounds of camphor with acids are already known. The *hydrocobalticyanide* is a crystalline powder of the formula $2C_{10}H_{16}O,H_3Co(CN)_6,2H_2O$. Fenchone and carone also give compounds, both with ferrocyanic and ferricyanic acid. Mesityl oxide yields an amorphous compound with ferricyanic acid, and a crystalline powder with ferrocyanic acid; phorone yields a crystalline compound with ferrocyanic acid, benzylideneacetone forms an amorphous compound with ferricyanic acid, a powder consisting of small tablets with ferrocyanic acid, and a *platinichloride*, $2C_{10}H_{10}O,H_2PtCl_6,2H_2O$, which crystallises in thin, orange-yellow prisms. Dibenzylideneacetone yields an orange-coloured, amorphous compound with ferricyanic acid, and a cinnabar-red, amorphous powder with phosphotungstic acid. The hydrochloride has previously been described by Claisen and Ponder (*Annalen*, 1884, **223**, 142) as a red powder. In order to ascertain whether this compound was a salt or a chlorohydrin, the corresponding *dichloro*-derivative, $CHPh{:}CH{\cdot}CCl_2{\cdot}CH{:}CHPh$, was prepared by the action of phosphorus pentachloride on the hydrochloride, and crystallises in colourless, lustrous plates melting at 78°. Since this compound is colourless, it follows that the hydrochloride cannot have a similar constitution. The dichloride itself is coloured yellow by hydrochloric acid, probably owing to the formation of an unstable salt. Carvenone yields an amorphous compound with ferrocyanic acid and small needles with ferricyanic acid. Inactive dihydrocarvone yields with ferrocyanic acid a crystalline powder and with ferricyanic acid an amorphous film. Quinone dissolves in syrupy phosphoric acid and is precipitated by water. With phosphotungstic acid, it forms a *compound* which crystallises in six-sided tablets. Similar salts of substances containing quinonoid oxygen, such as aurin and fluorescein, have long been known. Dimethylpyrone, in addition to the compounds described by Collie and Tickle, appears to form a *dihydrochloride* when the hydrochloride is exposed to hydrogen chloride. The hydrochloride reacts with potassium ferrocyanide and ferricyanide, crystalline salts of the complex acids being precipitated. The pyrone also unites with cobalticyanic acid to form rhombic tablets, and with phosphotungstic acid to form small needles.

Several cases of the combination of unsaturated compounds containing an ethylene linking with complex acids have also been observed, and it appears probable that these compounds are also capable of forming salts. A. H.

Synthesis of Tertiary Cyclic Alcohols by the Aid of Magnesiumalkylhaloids. By Nicolai D. Zelinsky (*Ber.*, 1901, **34**, 2877—2884. Compare Barbier, Abstr., 1899, i, 323; Grignard, 1900, i, 382; this vol., i, 250, 263; Blaise, this vol., i, 317).—The following method is recommended for the preparation of tertiary cyclic alcohols.

An alkyl iodide (1 mol.) is carefully added to magnesium (1 atom.), covered with dry ether, and to this mixture an ethereal solution of the cyclic ketone (1 mol.) is gradually run in. Acidified water is added, and the ethereal solution separated, and dried with potassium carbonate.

1-*Methyl*cyclo*hexanol*-1, $CH_2{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}{>}CMe\cdot OH$, obtained from *cyclo*hexanone, is a colourless oil, distils at 156—158°, and has a sp. gr. 0·9194 at 26°/4°, and n_D 1·4558 at 26°.

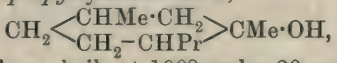
1 : 3-*Dimethyl*cyclo*hexanol*-3, from 1-methyl*cyclo*hexanone-3, distils at 67—68° under 16 mm. pressure, has a sp. gr. 0·8983 at 23°/4°, n_D 1·4523 at 23°, and is slightly dextrorotatory.

1-*Methyl-3-ethyl*cyclo*hexanol*-3 distils at 80—81° under 16 mm. pressure, and has a sp. gr. 0·8995 at 26°/4°, n_D 1·4545 at 26°, and $[\alpha]_D$ +1·48°.

1-*Methyl-3-propyl*cyclo*hexanol*-1 distils at 94—96° under 18 mm., or at 198—200° under atmospheric pressure, and has a sp. gr. 0·8903 at 24°/4°, and n_D 1·4566 at 24°. The corresponding iso*propyl* derivative boils at 81—83° under 14 mm., or at 186—188° under atmospheric pressure, but is always accompanied by a considerable amount of a hydrocarbon distilling at 152—153° under 14 mm. pressure.

A *hydrocarbon*, $C_{20}H_{38}$, boiling at 260°, is formed by the action of acetone on magnesium, dry ether, and 1-methyl*cyclo*hexyl-3 iodide and subsequent treatment of the product with acidified water.

1 : 3-*Dimethyl*-4-iso*propyl*cyclo*hexanol*-3,



$$CH_2{<}\begin{matrix}CHMe\cdot CH_2\\ CH_2-CHPr\end{matrix}{>}CMe\cdot OH,$$

obtained from menthone, boils at 100° under 20 mm. pressure, and has a sp. gr. 0·8952 at 25°/4° and $[\alpha]_D$ +12°22′. *d*-Fenchone yields *methylfenchyl alcohol*, $C_{10}H_{16}Me\cdot OH$, distilling at 100—102° under 22 mm., or at 208—209° under atmospheric pressure; it melts at 51—52°, and has $[\alpha]_D$ +11°. *Methylborneol*, obtained from ordinary camphor, melts at 154—156°, readily sublimes, distils at about 193°, and has $[\alpha]_D$ 30°79′ in alcoholic solution.

*Dimethyl*cyclo*propylcarbinol*, $\begin{matrix}CH_2\\ | \\ CH_2\end{matrix}{>}CH\cdot CMe_2\cdot OH$, from acetotrimethylene, distils at 123° under 740 mm. pressure, and has a sp. gr. 0·8791 at 24°/4°, and n_D 1·4309 at 24°. J. J. S.

Esterification of Glycerol. By Carl Boettinger (*Chem. Zeit.*, 1901, **25**, 795—797 and 811—812).—Pure glycerol has been mixed with known weights of the following acids: tartaric, succinic, malic, maleic, fumaric, citric, formic, acetic, chloroacetic, glycollic, and glyoxylic acids. Each mixture was left at the ordinary temperature for some time and then the amount of standard alkali required to neutralise the unesterified acid determined. Similar experiments were carried out (1) with the addition of one to two drops of hydrochloric acid, (2) at a higher temperature. The esterification was accelerated by both these methods. J. J. S.

Nitromannitol and Nitrocellulose. By LEO VIGNON and F. GERIN (*Compt. rend.*, 1901, 133, 515—517).—Pentanitromannitol and hexanitromannitol, obtained by the action of sulphuric and nitric acids on mannitol, readily reduce Fehling's solution, and thus resemble the nitrocelluloses (Abstr., 1900, i, 589, 628, 629); they have no action on Schiff's reagent, however, and in this respect differ from the nitrocelluloses. A further difference is found in the fact that whereas the nitrocelluloses give oxycelluloses when treated with ferrous chloride, the nitromannitols yield mannitol, which has no reducing power. The cupric reducing power of nitromannitol is greater than that of dextrose, but is not due to the presence of mannose. C. H. B.

Preparation of Alkyl and Aryl Carbonates. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 117624; Eng. Pat. 530 of 1900).—The additive *compound*, $CO(C_5H_7ON_2PhCl)_2$, of antipyrine with carbonyl chloride reacts with alcohols and phenols, yielding the corresponding carbonates; methyl and *n*-propyl chlorocarbonates are produced by the use of methyl and *n*-propyl alcohols respectively. *Methyl-*n*-propylcarbinyl chlorocarbonate*, $CHMePr^{\alpha}\cdot O\cdot COCl$, an oil boiling at 68° under 26 mm., and at 140—145° under atmospheric pressure, is obtained from methyl-*n*-propylcarbinol, whilst *menthyl chlorocarbonate* boiling at 105—106° under 12 mm. pressure results from the interaction of antipyrine carbonyl chloride and menthol. *Guaiacol chlorocarbonate*, prepared in a similar manner, is a colourless oil boiling at 112° under 25 mm. pressure.

The *compound* $OMe\cdot C_5NH_5\cdot CO\cdot C_5NH_5Cl$, produced from methyl chlorocarbonate and pyridine in benzene solution, yields alkyl or aryl carbonates when treated with water, alcohols, or phenols. Dimethyl carbonate is obtained by the action of water, and methyl benzyl carbonate results from the action of benzyl alcohol on this additive compound.

The *compound* $CO(O\cdot C_6H_4\cdot CO_2Ph)_2$ is produced from salol and the additive compound of pyridine and salol chlorocarbonate, the compound $OEt\cdot CO\cdot O\cdot C_6H_4\cdot CO_2Ph$ being obtained by the action of alcohol on the same pyridine derivative. G. T. M.

Alkyl Carbonates. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 117625. Compare preceding abstract).—*Methyl-*n*-propylcarbinyl carbonate*, $CO(O\cdot CHMePr^{\alpha})_2$, a colourless oil having a slightly aromatic odour and boiling at 205—207°, results from the action of methyl-*n*-propylcarbinol on the additive compound of pyridine and carbonyl chloride. In a similar manner, the dimethyl and diethyl carbonates are obtained by the action of the corresponding alcohols on this pyridine derivative. G. T. M.

Carbamates of the Secondary Alcohols. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 120863. Compare D.R.-P. 114396).—The *chlorocarbonates* of methylethyl-, diethyl-, methylpropyl-, methyl*iso*propyl-, ethylpropyl-, ethyl*iso*propyl-, methylbutyl-, and dipropyl-carbinols are liquids having an irritating odour and boil respectively at 121—122°, 131—133°, 140—141°, 130—132°, 141—143°, 144—146°, 144—146°, and 157—159°. Methyl *iso*propyl-carbamate may be obtained either by heating methyl *iso*propylchloro-carbonate with ammonia in an indifferent solvent, or by slowly adding carbamide hydrochloride to methyl *iso*propylcarbinol; it melts at 86—87°. The corresponding methylbutyl compound crystallises in white needles and melts at 56°. These two methods are applicable to the preparation of the homologous alkyl carbamates. G. T. M.

Carbamates of the Secondary Alcohols. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 120864. Compare preceding abstract).—The carbamates of the secondary alcohols may be obtained by treating the secondary alcohols with cyanogen chloride or cyanic acid dissolved in an indifferent solvent, and also by the action of ammonia on the corresponding dialkyl carbonates. The *dialkyl carbonates* obtained from methylethyl-, diethyl-, methylpropyl-, methyl*iso*propyl-, ethylpropyl-, ethyl*iso*propyl-, methylbutyl-, and dipropyl-carbinols are liquids boiling respectively at 178—180°, 205—207°, 208—210°, 205—207°, 233—234°, 227—228°, 239—240°, and 260—265°. G. T. M.

Carbamates of the Secondary Alcohols. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 120865. Compare preceding abstracts).—*Methyl-*n*-butylcarbinyl carbamate*, $NH_2\cdot CO_2\cdot CHMe\cdot CH_2Pr^{\alpha}$, the *urethane* of methyl-*n*-butylcarbinol, melts at 65—66°; its higher homologue, $NH_2\cdot CO_2\cdot CHEt\cdot CH_2Pr^{\alpha}$, melts at 80—81°; these compounds are prepared either by the action of urea nitrate on the corresponding secondary alcohols, or by the reactions indicated in the preceding abstracts. The *chlorocarbonates*, prepared from ethyl*iso*butyl-, methyl-*n*-butyl-, and methyl-*n*-pentyl-carbinols, boil respectively at 155—157°, 144—146°, and 154—156° under the ordinary pressure. The *dialkyl carbonates* obtained from ethyl*iso*butyl-, methyl-*n*-butyl-, and methyl-*n*-pentyl-carbinols boil at 250—255°, 228—230°, and 249—250° respectively. G. T. M.

Composition of Cocoa Butter. Preliminary Communication. By J. KLIMONT (*Ber.*, 1901, **34**, 2636).—Cocoa butter may be separated by fractional crystallisation from acetone into three fractions: 1. A mixture of palmitin and stearin melting at 70°. 2. Palmitic-oleic-stearic triglyceride, $C_{55}H_{104}O_6$, which melts at 31—32°, crystallises in nodules, and has the iodine number 28·9 and the saponification number 196·4. 3. A mixed glyceride, $C_{51}H_{96}O_6$, which melts at 26—27°, and has the iodine number 31·7 and the saponification number 210·5. A. H.

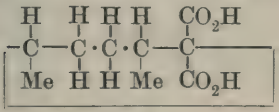
Action of Fuming Nitric Acid on Substituted Acrylic Acids. By A. WAHL (*Bull. Soc. Chim.*, 1901, [iii], **25**, 804—808).—The action of fuming nitric acid on ethyl crotonate takes place with difficulty, and results in the formation of a small quantity of *ethyl nitrocrotonate*, a pale yellow liquid boiling at 100—106° under 13 mm. pressure. When ethyl tiglate is treated with fuming nitric acid, fixation of the latter occurs, but no well-defined product seems to be formed. Ethyl *iso*lauronolate, when similarly treated, yields a *nitrate*, $C_{11}H_{19}O_5N$, which crystallises in colourless prisms melting at 79—80°, and regenerates the original ester on reduction with aluminium amalgam. From methyl cinnamate, a mixture of methyl *o*- and *p*-nitrocinnamates is obtained. N. L.

Constitution of α- and β-Nitrodimethylacrylic Esters. By Louis Bouveault and A. Wahl (*Bull. Soc. Chim.*, 1901, [iii], **25**, 808—817).—The experimental results described in this paper have been already noticed (this vol., i, 5). The question of the constitution of the potassium salt of ethyl β-nitrodimethylacrylate and analogous compounds is now discussed, the views of V. Meyer, Michael, Nef, and Hantzsch being referred to. N. L.

Camphoric Acid. X. Racemic Campholytic Acid and Racemic Dihydrohydroxycampholytic Acid. By William A. Noyes and W. M. Blanchard (*Amer. Chem. J.*, 1901, **26**, 281—292). —Racemic α-campholytic acid (Walker and Cormack, Trans., 1900, **77**, 380) boils at 127—128° under 14 mm. pressure, and forms crystals melting at 31°. When its hydrobromide is treated with sodium hydroxide, in addition to the regenerated acid, *racemic dihydrohydroxycampholytic acid* is produced, which crystallises in needles from ethyl acetate or water, and if warmed with dilute sulphuric acid is converted into β-campholytic acid. This acid can be resolved into its optically active components by fractional crystallisation of the strychnine salts; the *d*-acid thus obtained is identical with that prepared from aminodihydrocampholytic acid (Abstr., 1895, i, 295). By the action of bromine on racemic α-campholytic acid, dibromo-α-campholytic acid melting at 109° and dibromo-β-campholytic acid melting at 141° are produced.

Racemic dihydro-α-campholytic acid, $C_8H_{15}\cdot CO_2H$, obtained by reducing the hydriodide of *i*-α-campholytic acid with zinc dust, boils at 245—247°; its *amide* crystallises in needles and melts at 103—104°. *α-Bromodihydro-*i*-α-campholytic acid*, $C_8H_{14}Br\cdot CO_2H$, obtained by treating the acid with phosphorus pentachloride and warming the resulting chloride with bromine in a sealed tube, crystallises in needles and melts at 148°. By the action of alcoholic potassium hydroxide on the bromo-acid, or of barium hydroxide on its ester, Δ^5-*campholytic acid* is produced, which crystallises in needles, melts at 90—91°, and decolorises a potassium permanganate solution; when warmed with dilute sulphuric acid, it is not converted into β-campholytic acid. Δ^5-*Campholytic amide* crystallises in leaflets or small plates, and melts at 90°. E. G.

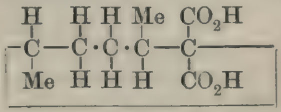
2 : 5-Dimethyl-1 : 1-Di- and -1-Mono-Carboxylic Acids of *cyclo*Pentane. By Johannes Wislicenus [with Kurt Peters, Otto Schramm, and Otto Mohr] (*Ber.*, 1901, **34**, 2565—2583).—When βε-dibromohexane (Schramm, Abstr., 1897, i, 262), boiling at 99—100° under 20 mm. pressure, is suspended in boiling alcohol, mixed with a slight deficiency of ethyl disodiomalonate, and heated until the mixture has become neutral in reaction, an oil is obtained boiling at 169—180° under 76 mm., or at 250—264° under the ordinary pressure, and with the composition of diethyl dimethyl*cyclo*pentanedicarboxylate. When this is hydrolysed with 20 per cent. alcoholic potash, a mixture of ester-acids, dicarboxylic acids, and monocarboxylic acids is obtained; these can be separated by means of their different solubility in light petroleum or water, or different volatility with steam. Each of them was shown to be related to one or other of two dicarboxylic acids, and the original ester must have been a mixture of the diethyl esters of these two acids; the pure esters were prepared by starting with the acids. The acids are stereoisomerides, being derived from stereoisomeric dimethyl*cyclo*pentanes in which the two methyl groups are respectively on the same side (*cis-cis*), and on opposite sides (*cis-trans*), of the pentamethylene ring, as is indicated by the formulæ



$$\begin{array}{ccccc} H & H & H & H & CO_2H \\ -C- & C\cdot & C\cdot & C- & C- \\ Me & H & H & Me & CO_2H \end{array}$$

Cis-cis.

and

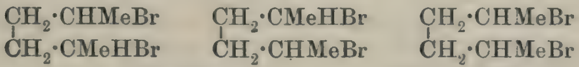


$$\begin{array}{ccccc} H & H & H & Me & CO_2H \\ -C- & C\cdot & C\cdot & C- & C- \\ Me & H & H & H & CO_2H \end{array}$$

Cis-trans.

They were identified by eliminating one carboxyl group from each by heating it at 190—210°. Under these circumstances, one of them yielded two (stereoisomeric) monocarboxylic acids, the other only one; it is obvious from the formulæ that these must have been the *cis-cis* and *cis-trans*-dicarboxylic acids respectively.

The $\beta\epsilon$-dibromohexane employed can be separated into a solid and a liquid part by cooling it to 0° and inoculating it with a crystal of the solid, obtained by cooling a small portion with solid carbon dioxide and ether (compare Demjanoff, Abstr., 1891, 160). The solid *$\beta\epsilon$-dibromohexane* melts at 38·2°, boils at 98—99° under 16—17 mm. pressure, and has a sp. gr. 1·5315 at 56°. The liquid isomeride, when purified as far as possible, boiled at 94° under 13—14 mm. pressure, and had the sp. gr. 1·5256 at 56°, and 1·5822 at 11·9°. Now it is possible, theoretically, for $\beta\epsilon$-dibromohexane to exist in several stereoisomeric forms, as the following formulæ indicate:—



$$\begin{array}{ccc} CH_2\cdot CHMeBr & CH_2\cdot CMeHBr & CH_2\cdot CHMeBr \\ | & | & | \\ CH_2\cdot CMeHBr & CH_2\cdot CHMeBr & CH_2\cdot CHMeBr \end{array}$$

Active forms. *Meso*-form.

When the condensation with ethyl disodiomalonate takes place, the two bromine atoms which are eliminated will presumably take up positions opposite to each other. In the case of the *meso* form, this will bring the two methyl groups to the same side of the pentamethylene ring which is formed, and so would give rise to a *cis-cis*-dimethyl*cyclo*pentane derivative. In the case of either of the two active forms, the two methyl groups will be brought to opposite sides of the ring, with consequent formation of a *cis-trans*-derivative. By actual experiment, it is found that the solid dibromohexane gives *cis-cis*-dimethyl*cyclo*pentane derivatives, and so it must possess the *meso*-configuration. On the other hand, the liquid isomeride gives *cis-trans*-derivatives, and must therefore be regarded as a racemic mixture of the active forms.

The following new compounds were prepared:—

cis-cis-2:5-*Dimethyl*cycl*opentane derivatives.*—1:1-*Dicarboxylic acid*, $C_5H_6Me_2(CO_2H)_2$, melting and decomposing at 192—194°; *silver* salt; *calcium* salt, with $6H_2O$; *diethyl ester*, boiling at 138° under 20 mm.

pressure, with a sp. gr. 1·019. The acid, when heated, yields two 1-*monocarboxylic acids*, $C_5H_7Me_2 \cdot CO_2H$, melting at 26—30° (*silver* salt analysed), and 75—77° (*silver* salt and *calcium* salt, with $2H_2O$, analysed). The ester, when hydrolysed, yields mainly an *ester-acid*, $CO_2Et \cdot C_5H_6Me_2 \cdot CO_2H$, melting at 81·5°; *silver* salt analysed. This yields, when heated, an *ethyl* 1-*carboxylate*, $C_5H_7Me_2 \cdot CO_2Et$, which boils at 187—188°, has a sp. gr. 0·920, and can be hydrolysed to the monocarboxylic acid melting at 75—77°.

cis-trans-2 : 5-*Dimethylpentane derivatives*.—1 : 1-*Dicarboxylic acid*, melting and decomposing at 204—205°; *silver* salt; *calcium* salt, with $\frac{1}{2}H_2O$; yields, on esterification, the *diethyl ester*, boiling at 133° under 20 mm. pressure and with a sp. gr. 1·022, and the *ester-acid*, which melts at 54° (*silver* salt analysed), and, when heated, yields the *ethyl* 1-*carboxylate*. This boils at 190°, has a sp. gr. 0·926, and can be hydrolysed to the 1-*carboxylic acid*, which is also formed when the dicarboxylic acid is heated. This acid melts at 49—50°; its *silver* salt and *calcium* salt, with $1H_2O$, were analysed. C. F. B.

Rubidium Racemate. By GRÉGOIRE N. WYROUBOFF (*Chem. Centr.*, 1901, ii, 764; from *Bull. Soc. franç. Min.*, 1901, **24**, 270—273. Compare *ibid.*, **6**, 58, and Traube, *Jahrb. Min.*, [ii], *Beilageband*, **10**, 795).—Rubidium racemate, $C_4H_4O_6Rb_2,2H_2O$, crystallises at temperatures below 20° in large, monoclinic plates [$a:b:c = 0·9024:1:0·6323$; $ac = 91°42'$.] E. W. W.

Constitution of Citric Acid Derivatives. By GUIDO SCHIAVON (*Gazzetta*, 1901, **31**, i, 536—544).—The author has prepared various salts by partially or completely neutralising citric acid with a base or with two bases in the proportion of two equivalents of the one to one of the other, the salts obtained being examined, especially as regards their crystalline form and rotatory power, with the view of elucidating their constitution.

The diammonium hydrogen salt separates from its concentrated solution in crystals melting at 150°. [PANEBIANCO finds that these crystals occur only in dextro-hemihedral forms and not in equal proportions of the dextro- and lævo-forms as was stated by Heusser.] The solution of these crystals is optically inactive, but after the action of *Penicillium glaucum* in presence of nutritive salts, it becomes slightly lævorotatory. The monoclinic form of this salt, described by Heldt in 1843, could not be prepared. The diammonium salt is obtained in deliquescent rhombic crystals containing $\frac{1}{2}H_2O$ when powdered citric acid is neutralised with concentrated ammonia solution. On account of the optical activity conferred on this salt by *Penicillium*, the author ascribes to it the asymmetric formula,

$$CO_2NH_4 \cdot CH_2 \cdot C(OH)(CO_2NH_4) \cdot CH_2 \cdot CO_2H.$$

The monoammonium dihydrogen salt separates from its solution in triclinic, deliquescent crystals, the solution of which is optically inactive and remains so after the action of *Penicillium*. The salt hence probably contains no asymmetric carbon atom and has the formula

$$OH \cdot C(CH_2 \cdot CO_2H)_2 \cdot CO_2NH_4.$$

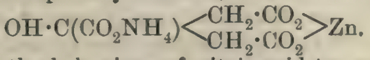
The disodium monoammonium salt, obtained either by neutralising monoammonium citrate with sodium carbonate or by neutralising two-thirds of a given quantity of citric acid with sodium carbonate and the remaining third with ammonia, is slightly lævorotatory in concentrated solution and hence has probably the constitution

$$CO_2Na{\cdot}CH_2{\cdot}C(OH)(CO_2Na){\cdot}CH_2{\cdot}CO_2NH_4.$$

The disodium salt from which the last-named is formed must therefore have the formula $CO_2Na{\cdot}CH_2{\cdot}C(OH)(CO_2Na){\cdot}CH_2{\cdot}CO_2H$.

By the addition of citric acid to the neutral optically inactive trisodium salt, a disodium hydrogen citrate is obtained, which is also optically inactive and has the constitution $OH{\cdot}C(CH_2{\cdot}CO_2Na)_2{\cdot}CO_2H$.

The dizinc monoammonium salt, formed by the action of ammonia on the trizinc compound, is obtained as a white, insoluble deposit containing $2H_2O$ and is optically inactive, its formula being



$$OH{\cdot}C(CO_2NH_4){<}\begin{matrix}CH_2{\cdot}CO_2\\CH_2{\cdot}CO_2\end{matrix}{>}Zn.$$

Examination of the behaviour of citric acid towards indicators gave the following results. Litmus, phenolphthalein, rosolic acid, and tropæolin-OOO indicate neutrality when the three carboxylic hydrogen atoms of citric acid have been replaced. Cochineal and congo-red are neutral towards salts containing one unreplaced carboxylic hydrogen, whilst tropæolin-OO has a neutral reaction with citrates, in which only one-third of the carboxylic hydrogen has been replaced; methyl-orange apparently acts like tropæolin-OO, but does not lend itself well to use with citric acid. Lacmoid behaves similarly to the indicators given in the first group above, but when the acid solution is neutralised to the extent of two-thirds, it assumes a more violet colour with a red fluorescence. T. H. P.

[Manganese Citrate.] By Frederick B. Power (*Pharm. J.*, 1901, [iv], **13**, 135—137).—Manganese citrate, $Mn_3(C_6H_5O_7)_2,9H_2O$, was first prepared by Kammerer (*Annalen*, 1868, **148**, 314) by heating together solutions of manganous acetate and citric acid. The author has obtained the same salt by the action of citric acid on manganous carbonate. E. G.

Iron Citrate and Iron Ammonium Citrate. By C. Martinotti and L. Cornelio (*Chem. Centr.*, 1901, ii, 626, 764; *from Boll. Chim. Farm.*, 1901, **40**, 445—454 and 481—489).—Iron citrate,

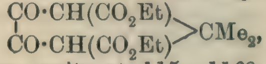
$$(C_6H_{6\frac{1}{2}}O_7)_2Fe_2(OH)_3,3H_2O,$$

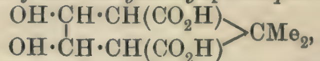
cannot be regarded as a normal citrate since it has an acid reaction, loses $3H_2O$ at 100°, is completely dehydrated only at 150°, and combines with 3 mols. of ammonia. Monoammonium iron citrate,

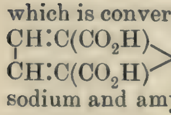
$$(C_6H_6O_7)_2(NH_4)Fe_2(OH)_3,3H_2O,$$

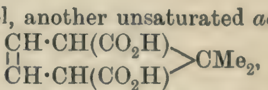
prepared in the same way as the diammonium salt and also by the oxidation of the corresponding ferrous ammonium citrate, is very slightly deliquescent and far less soluble than the di- and tri-ammonium salts. The diammonium salt, $(C_6H_{5\frac{1}{2}}O_7)_2(NH_4)_2Fe_2(OH)_3,3H_2O$, is browner than the monoammonium iron citrate. The triammonium salt, $(C_6H_5O_7)_2(NH_4)_3Fe_2(OH)_3,3H_2O$, is prepared by treating iron citrate with ammonia until it shows an alkaline reaction.

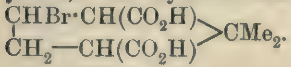
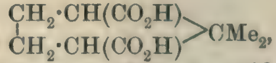
The green iron ammonium citrate, obtained by adding ammonium citrate or citric acid to the reddish-brown iron triammonium citrate, is really a mixture of iron citrate, $(C_6H_5O_7)_2Fe_2$, with ammonium citrate and usually also with citric acid. Ferrous citrate, $C_6H_6O_7Fe,H_2O$, is a greenish-white powder and dissolves very readily in ammonia with a slight development of heat, forming a rather unstable ferrous ammonium citrate, $C_6H_5O_7(NH_4)Fe$, which is easily oxidised to diammonium ferric citrate. E. W. W.

Complete Synthesis of *apo*Camphoric Acid (Camphopyric Acid). By Gustav Komppa (*Ber.*, 1901, **34**, 2472—2475).—ββ-Dimethylglutaric acid (Abstr., 1899, i, 573) condenses with ethyl oxalate to form *ethyl diketo*apo*camphorate*,  $\begin{array}{l}\text{CO·CH(CO}_2\text{Et)}\\ \text{CO·CH(CO}_2\text{Et)}\end{array}\!>\!\text{CMe}_2$, which melts at 98°; the analogous *methyl* ester melts at 115—116°. On reduction, the acid yields *dihydroxy*apo*camphoric acid*,


$$\begin{array}{l}\text{OH·CH·CH(CO}_2\text{H)}\\ \text{OH·CH·CH(CO}_2\text{H)}\end{array}\!>\!\text{CMe}_2,$$

which is converted by hydriodic acid into an unsaturated *acid*, probably  $\begin{array}{l}\text{CH:C(CO}_2\text{H)}\\ \text{CH:C(CO}_2\text{H)}\end{array}\!>\!\text{CMe}_2$, melting at 203—209°; when this is reduced with sodium and amyl alcohol, another unsaturated *acid*,


$$\begin{array}{l}\text{CH·CH(CO}_2\text{H)}\\ \text{CH·CH(CO}_2\text{H)}\end{array}\!>\!\text{CMe}_2,$$

is obtained, which forms triclinic tablets, melts at 203—205°, and yields, with hydrobromic acid at 120—130° the *additive* compound  $\begin{array}{l}\text{CHBr·CH(CO}_2\text{H)}\\ \text{CH}_2\text{—CH(CO}_2\text{H)}\end{array}\!>\!\text{CMe}_2$. The latter, on reduction with zinc dust and acetic acid, gives apo- or nor-*camphoric acid*,  $\begin{array}{l}\text{CH}_2\text{·CH(CO}_2\text{H)}\\ \text{CH}_2\text{·CH(CO}_2\text{H)}\end{array}\!>\!\text{CMe}_2$, melting at 160—170°, and identical with *meso*camphopyric acid (Marsh and Gardner, Trans., 1896, **69**, 79). The acid was resolved into its *cis*- and *trans*-forms, and the *cis*-form identified by its melting point (203·5—204·5°), and that of its anhydride (174—175°) and anil (211°). This synthesis confirms Bredt's formulæ for camphor, camphene, and fenchocamphorone. W. A. D.

Molecular Weight of Chloral Hydrate at the Boiling Point. By Robert de Forcrand (*Compt. rend.*, 1901, **133**, 474—476).—If Berthelot's values of 21900 cal. and 5500 cal. be adopted for the molecular heats of evaporation and fusion of chloral hydrate, the value of $(L+S)/T$ is 74·1, in place of the usual constant 30. If the compound were completely dissociated, the value 60 should be obtained. The values given for the latent heats, however, include the heat of combination, 6230 cal., and by subtracting this from $L+S$, the quotient $(L+S)/T$ is 57·3. This indicates almost complete dissociation and by the converse calculations, adopting the value 30 for the constant, the value 86·6 is obtained for the molecular weight, 82·75 corresponding with complete dissociation. As the constants for water are accurately known, the author attempts further to separate the calculation into two parts, (1) that due to water, (2) that due to the chloral, and so obtain the value 31·4 for $(L+S)/T$ in the case of the anhydrous compound. Although the results can only be approximate, they indicate 4 or 5 per cent. of undissociated hydrate at the boiling point (this vol., ii, 372, 594). L. M. J.

Researches on the Acetals. By MARCEL DELÉPINE (*Ann. Chim. Phys.*, 1901, [vii], **23**, 378—416 and 482—498).—A detailed account of work already published (compare this vol., i, 3, 254, 314, 365 ; ii, 6). G. T. M.

Action of Barium Hydroxide and of Sodium on several Aldehydes. By ANTON LEDERER (*Monatsh.*, 1901, **22**, 536—544).—Barium hydroxide converts acetaldehyde and crotonaldehyde in aqueous solution into resins. *iso*Butaldehyde, when heated in a sealed tube with barium hydroxide and a small quantity of water, is transformed nearly quantitatively into *iso*butyl alcohol and *iso*butyric acid. The formation of an alcohol and acid from an aldehyde (Cannizzaro's reaction) has never been previously observed in the case of an aldehyde in which hydrogen is attached to the α-carbon atom (compare Lieben, this vol., i, 449). On treating *iso*valeraldehyde with barium hydroxide, α-*iso*propyl-β-*iso*butylacraldehyde is formed (Kohn, Abstr., 1896, i, 461).

Metallic sodium (or sodium hydroxide) converts *iso*butaldehyde mainly into octoglycol *iso*butyrate (Brauchbar and Kohn, Abstr., 1898, i, 353), a small quantity of *iso*butyl alcohol being formed at the same time. *iso*Valeraldehyde is transformed by metallic sodium into an ester of *iso*valeric acid and the glycol $C_{10}H_{22}O_2$ (see following abstract). K. J. P. O.

Condensation Products of *iso*Valeraldehyde. By HUGO ROSINGER (*Monatsh.*, 1901, **22**, 545—560).—*iso*Valeraldehyde was found by Kohn (Abstr., 1896, i, 461, and 1897, i, 396) to form three condensation products, an unsaturated aldehyde, *iso*valeraldol, and a compound $(C_5H_{10}O)_x$ to which Reychler (Abstr., 1897, i, 549) assigned the formula $C_{10}H_{20}O_2$. The author finds that this *substance* is best prepared by boiling the aldehyde with solid potassium hydroxide and has the formula $C_{15}H_{30}O_3$. It is the ester of *iso*valeric acid and the *glycol* $C_{10}H_{22}O_2$; the latter is obtained by hydrolysing the ester with alcoholic potash and is a viscous oil boiling at 143° under 15 mm. pressure ; it yields a *diacetate*, $C_{10}H_{20}O_2Ac_2$, as an oil boiling at 145° under 18 mm. pressure. When heated with acetic anhydride, the ester yields no acetyl derivative, but when treated with acetic anhydride and sulphuric acid, it gives a *monoacetate*, $C_{15}H_{29}O_3Ac$, which is an oil boiling at 150° under 18 mm. pressure. For the ester, the author suggests the constitution $CH_2Pr^\beta\cdot CO_2\cdot CH_2\cdot CHPr^\beta\cdot CH(OH)\cdot CH_2Pr^\beta$. K. J. P. O.

Condensation of α-Hydroxybutaldehyde with Acetaldehyde. By JULIUS ROESLER (*Monatsh.*, 1901, **22**, 527—535).—When a mixture of α-hydroxy*iso*butaldehyde and acetaldehyde in molecular proportion is left in contact with $3N$ potassium hydroxide for three weeks, condensation to an aldol takes place. The *aldol*,

$$OH\cdot CMe_2\cdot CH(OH)\cdot CH_2\cdot CHO,$$

boils at 125—127° under 16 mm. pressure, and can be obtained in white crystals melting gradually at 70°. It reduces ammoniacal silver nitrate, and on distillation at the ordinary pressure is converted into an unsaturated aldehyde. The *diacetate*, $C_6H_{10}O_5Ac_2$, is an oil boiling at 140° under 16 mm. pressure; the *oxime*, $C_6H_{13}O_3N$, is an oil. On reducing the aldol with aluminium amalgam, an oil was obtained which could not be purified; it yields a *diacetate*, $C_6H_{12}O_5Ac_2$, which is an oil boiling at 162—164° under 16 mm. pressure, and is probably the diacetate of a hexylglycerol. K. J. P. O.

Compounds of the Alkali Metals and Cyclic Aminoketones. Emanuel Merck (D.R.-P. 119506).—Tropinone, triacetoneamine, and vinyldiacetoneamine suspended in dry ether or benzene yield sodium or potassium derivatives on treatment with the metal in the form of wire or ribbon. These products form yellow, hygroscopic powders, and are immediately decomposed by water, regenerating the aminoketones.

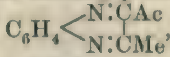
G. T. M.

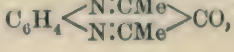
$\beta\gamma\delta$-Triketopentane. I. By Franz Sachs and Hermann Barschall (*Ber.*, 1901, **34**, 3047—3054).—*Diacetyl-4-dimethylaminophenylazomethine* (*triketopentane-γ-p-dimethylaminoanil*), $NMe_2\cdot C_6H_4N:CAc_2$, obtained by condensing acetylacetone with nitrosodimethylaniline in alcoholic solution in the presence of sodium hydroxide, and cooling the product to −20°, crystallises from light petroleum in orange-yellow crystals, and melts at 73°; it is very soluble in the other organic solvents, and has a yellow vapour.

$\beta\gamma\delta$-Triketopentane hydrate, $COMe\cdot C(OH)_2\cdot COMe$, is prepared by hydrolysing the preceding compound with 10 per cent. sulphuric acid, extracting the product with ether, distilling the extract under 30 mm. pressure until an orange-yellow oil, *triketopentane*, is obtained, and allowing this to take up moisture by exposure to the atmosphere; it forms well-defined, colourless, rhombic prisms melting indefinitely from 32—50°. This hydrate crystallises from benzene without losing the elements of water, and is readily soluble in the other organic solvents with the exception of light petroleum; it slowly decomposes and becomes liquid when kept in a desiccator. It reduces potassium permanganate in the cold without producing a precipitate of the dioxide; ammoniacal silver nitrate and chromic acid are also readily reduced; Fehling's solution and copper acetate yield cuprous oxide even in the cold, whilst metallic copper is precipitated from a boiling solution of the sulphate. The dihydrate reddens litmus.

$\beta\gamma\delta$-Triketopentane, $COMe\cdot CO\cdot COMe$, has not hitherto been obtained completely free from the hydrate; it is the first and simplest example of the straight chain consecutive triketones.

Triketopentane bis-phenylhydrazone, $C_5H_6O(:N\cdot NHPh)_2$, formed in dilute alcoholic solutions of its generators with or without the addition of acetic acid, crystallises from alcohol in orange needles with a blue reflex and melts at 156°. The *dianil*, $C_5H_6O(:NPh)_2$, is obtained in prisms and melts at 157·5°; it is somewhat unstable and soon develops an odour of carbimide, whilst the melting point falls.

2 : 3-*Acetylmethylquinoxaline*,  $C_6H_4<\begin{matrix}N:CAc\\ \vert\\ N:CMe\end{matrix}$, or less probably



$$C_6H_4<\begin{matrix}N:CMe\\N:CMe\end{matrix}>CO,$$

prepared by the interaction of *o*-phenylenediamine hydrochloride and triketopentane in the presence of sodium acetate, crystallises from alcohol in pale yellow needles and melts at 86·5°; it dissolves in concentrated sulphuric acid to a deep yellow solution. G. T. M.

Behaviour of Carbohydrates with Hypochlorites. By WALTER BRAEUTIGAM (*Chem. Centr.*, 1901, ii, 680—681; from *Pharm. Zeit.*, **46**, 636—638).—When 20 parts of bleaching powder are triturated with 2 of dextrose, the mixture becomes moist, the temperature rises to 125°, steam is given off copiously, and a solid mass consisting of calcium carbonate and calcium oxalate is ultimately obtained. A violent action also occurs when the filtrate from a mixture of 20 parts of bleaching powder with 100 of water is treated with 2 parts of dextrose at 50° and the same products are formed; but when mixed in the cold the temperature rises to about 30°; the product consists mainly of calcium carbonate, with only a small quantity of oxalate, and a similar result is obtained when dilute solutions of hypochlorite are employed. The carbonic acid may possibly be derived from the decomposition of formic acid. Generally speaking, the members of the glucose and sucrose groups are decomposed by cold concentrated solutions of hypochlorites forming carbon dioxide, oxalic acid, and water, whilst the members of the cellulose and melitose groups are only attacked at 60—70°, forming dextrose, which is then decomposed either into carbon dioxide, oxalic acid, and water, or into carbon dioxide and water, according to the concentration of the solution.

E. W. W.

Derivatives of Dextrose and Galactose. By A. COLLEY (*Ber.*, 1901, **34**, 3205—3207).—This paper supplements that of Koenigs and Knorr on the same subject (this vol., i, 369). Tetracetylbromodextrose is best prepared by the action of acetyl bromide on dextrose in a sealed vessel at −10°. Tetracetylchlorodextrose is converted by silver acetate in acetic acid solution into the pentacetyldextrose melting at 131°, but with silver sulphate in the same solution it yields the oppositely active pentacetyldextrose melting at 111·8°.

W. A. D.

Isomeric Acetyl Halogen Derivatives of Dextrose, and the Synthesis of Glucosides. By EMIL FISCHER and E. FRANKLAND ARMSTRONG (*Ber.*, 1901, **34**, 2885—2900. Compare Abstr., 1894, i, 3; this vol., i, 257).—α-Tetracetylchlorodextrose is readily transformed into the isomeric β-compound when its ethereal solution is shaken with a little powdered crystallised sodium carbonate.

Heptacetylchloromaltose, $C_{26}H_{35}O_{17}Cl$, obtained by the action of aqueous hydrochloric acid on octacetylmaltose at 15°, forms small, colourless prisms, and melts at 64—66°.

Heptacetyl-β-methylmaltoside, obtained when the preceding compound is shaken with methyl alcohol and silver carbonate, crystallises in needles melting at 121—122° (corr.), and on hydrolysis with baryta water yields *β-methylmaltoside*, which, so far, has not been obtained in a crystalline form. It dissolves readily in water, but is very sparingly soluble in organic solvents, does not reduce Fehling's solution except after hydrolysis with acids, is strongly dextrorotatory, and on treatment with emulsin is converted into maltose, whereas yeast enzyme transforms it into dextrose and β-methylglucoside.

Tetracetyl-β-phenylglucoside, $C_{20}H_{24}O_{10}$, obtained by the action of sodium phenoxide (2 mols.) on β-tetracetylchlorodextrose, crystallises from alcohol in large, prismatic needles, melts at 127° (corr.), has a bitter taste, is very sparingly soluble in water, and has $[\alpha]_D\ -29{\cdot}04°$ at 20°. On hydrolysis with baryta water, it yields β-phenylglucoside which has $[\alpha]_D\ -71{\cdot}0°$ at 20° (compare Michael, *Amer. Chem. J.*, 1879, i, 307).

Tetracetyl-β-naphthylglucoside, $C_{24}H_{26}O_{10}$, crystallises in needles melting at 135—136° (corr.). J. J. S.

Measurement of the Rotatory Power of Sugar, its Variation with Temperature and with the Wave-length of the Light used. By Henri Pellat (*Ann. Chim. Phys.*, 1901, [vii], **23**, 289—316).—The quantity of sugar required to be dissolved to give 100 c.c. of solution at 20°, which in a 20 cm. tube (at 20°) rotates the plane of polarisation of the sodium *D* line through 21·67°, is 16·284 grams (or, corrected for the amount of ash left by the sugar examined, 16·275 grams). This gives for the specific rotation, $[\alpha]_D$, 66·536° at 20°, which is almost identical with the value (66·538°) reported by Mascart and Bénard to the *Commission pour l'unification des méthodes d'analyse des alcools et des sucres.* The variation of the rotation (measured in a glass tube) with the temperature, between 14° and 30°, is expressed by $\alpha_D^{20} = \alpha_D^t\,[1 + 0{\cdot}00037\,(t-20)]$. For the determination of the variation with the wave-length, the bright lines of various metals produced by the analysis of an arc light by the spectroscope were used. From the results obtained, it is clear that these cannot be represented by the inverse ratio of the squares of the wave-lengths, but the rotation for any particular wave-length can be found from the formula $\alpha_\lambda = \alpha_D(A/\lambda^2 + B/\lambda^4)$, where λ is the wave-length, and $A = 0{\cdot}325483$, and $B = 0{\cdot}00757003$, α_D, the rotation for the sodium *D* line, being accurately known. J. McC.

Mixed Esters of Cellulose and the Behaviour of Cellulose towards Nitrating Acids. By Charles F. Cross, Edward J. Bevan, and R. Leonard Jenks (*Ber.*, 1901, **34**, 2496—2499).—Contrary to the generally accepted view that the sulphuric acid used in nitrating cellulose exercises a merely dehydrating influence, it is shown that the acid initially combines with the fibre simultaneously with the nitric acid to form a mixed nitrate-sulphate ; after the product is washed with cold water until the washings are neutral, it contains considerable quantities of combined sulphuric acid, the proportion of the latter diminishing with the time of nitration, and especially with the percentage of water present in the nitrating mixture. When the nitration lasted only 7 minutes, and a mixture of sulphuric and nitric acids in the proportion 3 : 1 was used, no water being present, the product contained 4·62 per cent. of sulphuric acid ; with 10·13 per cent. of water present, the percentage of combined sulphuric acid was only 2·56.

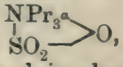
The sulphuric groups present are largely removed by hydrolysis when the cellulose nitrate is purified by boiling with water, and also by means of acetone containing sufficient water to prevent its acting as a solvent. W. A. D.

Researches on Caramel. IV. Decomposition Products of Caramelan. By FERDINAND STOLLE (*Zeit. Ver. deut. Zuckerind.*, 1901, 836—838).—One hundred grams of caramelan were heated for 18 hours on the water-bath with 1 litre of 3 per cent. hydrochloric acid, the products being 30 grams of a brownish-red, insoluble substance, and a hexose which gives an osazone crystallising in spherical aggregates of yellow needles melting at 197°, but which has not yet been identified.

T. H. P.

A Trimethyltriose. By CARL D. HARRIES and PAPPOS (*Ber.*, 1901, **34**, 2979—2980).—A *trimethyltriose* (*dihydroxydihydromesityl oxide*), $OH{\cdot}CMe_2{\cdot}CH(OH){\cdot}COMe$, is obtained as an oil on oxidising mesityl oxide, suspended in acetone, with cold potassium permanganate solution (Sachs, this vol., i, 272), and saturating the filtered and concentrated aqueous extract with potassium carbonate; it boils at 109° under 19 mm. pressure, and has a sp. gr. 1·077 at 22°. The new triose is a pale yellow, syrupy liquid having an odour of burnt sugar; it reduces Fehling's solution even in the cold, and dissolves in the ordinary organic solvents. The yield is 60 per cent. of the theoretical. The substance readily decomposes into acetone and acetol even on distillation under reduced pressure, the fraction obtained between 50—100° under 20 mm. pressure yielding acetol semicarbazone with semicarbazide, and the osazone of methylglyoxal with phenylhydrazine.

G. T. M.

Action of Hydrogen Peroxide on Fatty Amines. II. By LEONARD MAMLOCK and RICHARD WOLFFENSTEIN (*Ber.*, 1901, **34**, 2499—2505. Compare Abstr., 1900, i, 209).—Tripropylamine oxide is formed by the propylation of either β-dipropylhydroxylamine or of hydroxylamine with propyl iodide and sodium propyloxide (compare Dunstan and Goulding, Trans., 1899, **75**, 793); when prepared by the action of hydrogen peroxide on tripropylamine, it is obtained in the form of a crystalline hydrate, $NPr_3^{a}(OH)_2$, which only loses its combined water on complete decomposition. The oxide is reduced by sulphur dioxide in hot aqueous solution to tripropylamine, but at 0° is converted into N-*hydroxytripropylsulphamic anhydride*,  $\left.\begin{array}{l}\mathrm{NPr_3^{a}}\\ \mathrm{SO_2}\end{array}\right>\mathrm{O}$, which separates in white, silky crystals, melts at 159°, and is also obtained by the action of sulphur trioxide on tripropylamine at 0°. Dipropylsulphamic acid, formerly obtained by the action of sulphur dioxide on dipropylhydroxylamine, is also formed by the decomposition with boiling water of the *chloride*, $NPr_2^{a}{\cdot}SO_2Cl$, produced by the action of sulphuryl chloride on dipropylamine.

The formation of β-ethyl*sec*.butylhydroxylamine from nitroethane and zinc ethyl (Bewad, Abstr., 1900, i, 629) is due to the former interacting in the *iso*nitro-form, thus:

$$\left.\begin{array}{l}\mathrm{CHMe}\\ \mathrm{N(OH)}\end{array}\right>\mathrm{O} + \mathrm{ZnEt_2} \longrightarrow \mathrm{CHMeEt{\cdot}NEt{\cdot}OH} + \mathrm{ZnO}.$$

Bewad's base yields, with sulphur dioxide in benzene solution, the amorphous *ethyl*sec.*butylsulphamic acid*, $C_4H_9\cdot NEt\cdot SO_2\cdot OH$, which melts at 89—93°. The formation of this confirms Bewad's view as to the nature of the base. W. A. D.

New Class of Nitroamines. By Antoine P. N. Franchimont [with Lublin] (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, **4**, 88—91. Compare Abstr., 1895, i, 445).—Aminoethyl alcohol combines with methyl chloroformate, producing *methyl hydroxyethylaminoformate*, $OH\cdot CH_2\cdot CH_2\cdot NH\cdot CO_2Me$, which is a colourless liquid, decomposing, on heating, into methyl alcohol and the internal anhydride of hydroxyethylaminoformic acid. The *ethyl* ester is a liquid which does not decompose on heating, and can be distilled under reduced pressure.

On treating hydroxyethylaminoformic anhydride (2-ketotetrahydrooxazole) with pure nitric acid, a stable *mononitro*-derivative is obtained, crystallising in long, lustrous needles and melting at 111°. When boiled with water, it decomposes quantitatively into carbon dioxide and *nitroaminoethyl alcohol*, $NO_2\cdot NH\cdot CH_2\cdot CH_2\cdot OH$, which is obtained as a syrupy liquid on evaporating the aqueous solution; with boiling dilute sulphuric acid, it yields glycol and nitrous oxide. The *mercury* salt, prepared by boiling an aqueous solution of the nitroamine with mercuric oxide, crystallises in needles; the *silver* salt, similarly prepared, in plates; both salts explode on heating.

By the action of dry ammonia on a benzene solution of the internal anhydride, a compound is obtained, which, when boiled with absolute alcohol, yields ammonia and *hydroxyethylnitrocarbamide*,

$$OH\cdot CH_2\cdot CH_2\cdot N(NO_2)\cdot CO\cdot NH_2;$$

this substance crystallises in glossy plates, melting at 86°, and in aqueous solution, gives a white precipitate with mercuric nitrate; with barium hydroxide, it decomposes into nitroaminoethyl alcohol, ammonia, and carbon dioxide. The above carbamide derivative can be titrated with potassium hydroxide in the presence of phenolphthalein, and behaves as a monobasic acid. K. J. P. O.

Detection of Amino-derivatives of Sugars. I. By H. Steudel (*Zeit. physiol. Chem.*, 1901, **33**, 223—224).—Phenylcarbimide (Paal, Abstr., 1894, i, 332) is recommended as a precipitant for amino-derivatives of sugars. With glucosamine, it yields a *product*, $C_{13}H_{16}O_5N_2$, which is deposited from dilute acetic acid in the form of large, rhombic crystals, turning brown at 200° and melting sharply at 210°. J. J. S.

Synthesis of $\alpha\gamma$-Diaminobutyric Acid. By Emil Fischer (*Ber.*, 1901, **34**, 2900—2906. Compare this vol., i, 191).—*Ethyl β-phthaliminoethylbromomalonate*,

$$C_6H_4{:}(CO)_2{:}N\cdot CH_2\cdot CH_2\cdot CBr(CO_2Et)_2,$$

obtained by the action of bromine on a chloroform solution of crude ethyl β-phthaliminoethylmalonate (Abstr., 1891, 1247) in sunlight, crystallises from alcohol, when cooled to −20°, in colourless, truncated prisms, melts at 76—78°, and decomposes at 220—230°. After hydrolysis with hydrobromic acid saturated at 0°, and subsequent heating at 140—150° for 45 minutes, it yields *α-bromo-γ-phthaliminobutyric* *acid*; this crystallises in colourless plates, melts at 154—156° (corr.), and is readily soluble in most organic solvents. When treated with anhydrous liquid ammonia or, better, with aqueous ammonia, it yields *α-amino-γ-phthaliminobutyric acid*, which crystallises from hot water in small plates melting and decomposing at about 197°. On hydrolysis with hydrochloric acid of sp. gr. 1·19 at 100°, the phthalimino-acid yields *αγ-diaminobutyric acid hydrochloride*. The *acid* is extremely hygroscopic and readily soluble in water, but only sparingly so in alcohol, ether, or light petroleum. Its aqueous solution has a strong alkaline action and readily absorbs carbon dioxide. The normal *oxalate*, $(C_4H_{10}O_2N_2)_2,C_2H_2O_4,2H_2O$, crystallises in large, colourless plates, and melts and decomposes at about 219°. The *nitrate*, *sulphate*, *hydrochloride*, and *platinichloride* are all readily soluble, the *aurichloride* is readily decomposed, and the phosphotungstate and mercurichloride form white precipitates. The *dibenzoyl* derivative,

$$NHBz \cdot CH_2 \cdot CH_2 \cdot CH(NHBz) \cdot CO_2H,$$

is formed when a considerable excess of benzoyl chloride is employed, and crystallises in small needles melting at 200—201°.

J. J. S.

Derivatives of Glycine. By EMIL FISCHER and ERNEST FOURNEAU (*Ber.*, 1901, **34**, 2868—2877).—This paper deals with molecular anhydrides of amino-acids as distinct from the bimolecular anhydrides or diacipiperazines, and in it the name glycyl is used for the radicle $NH_2 \cdot CH_2 \cdot CO$.

Glycylglycine hydrochloride, $NH_2 \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H,HCl,H_2O$, crystallises out as a mass of slender needles when glycine anhydride (diacipiperazine) is dissolved in and boiled for a minute with strong hydrochloric acid; when treated with aqueous alkalis, or, better, with moist silver oxide, it is converted into *glycylglycine*, which crystallises in lustrous leaflets and decomposes between 215° and 220°. The following derivatives of glycylglycine are described: a deep blue *copper* salt crystallising in needles; the *ethyl* ester, which crystallises from light petroleum in slender needles melting at 88—89° (corr.), and in aqueous solution rapidly regenerates the glycine anhydride at the ordinary temperature; the *hydrochloride* of the ester, which crystallises in lustrous needles, and melts and decomposes at 182° (corr.); and the *phenylcarbimide*, $NHPh \cdot CO \cdot NH \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$, which crystallises from water in slender, silky needles, melts and decomposes at 175° (corr.), and forms a crystalline *ethyl* ester, $C_{13}H_{17}O_4N_3$, melting at 165—166°. *Carbethoxyglycylglycine ethyl ester*,

$$CO_2Et \cdot NH \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2Et,$$

obtained by the action of ethyl chlorocarbonate on glycylglycine ethyl ester, crystallises from ethyl acetate in flat prisms, dissolves readily in hot water, alcohol, or benzene, melts at 87° (corr.), and when treated with liquid ammonia at the ordinary temperature or with alcoholic ammonia at 100° yields *carbamidoglycylglycine ethyl ester*, $C_7H_{13}O_4N_3$, which crystallises from alcohol or water in six-cornered leaflets, melts and decomposes at 183° (corr.), and gives the biuret reaction.

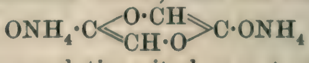
Similar compounds can be obtained from the ethyl ester of leucine and from alanine anhydride.

R. H. P.

The so-called *iso*Amides and True Amides. By Arthur Hantzsch and E. Voegelen (*Ber.*, 1901, **34**, 3142—3163).—Determinations of the molecular weight of glycolliminohydrin by the boiling point method, using absolute alcohol as solvent, agree with the formula $C_4H_{10}O_4N_2$, and not with the unimolecular formula

$$C_2H_5O_2N\,[=OH{\cdot}CH_2{\cdot}C(OH){:}NH]$$

(compare Eschweiler, Abstr., 1897, i, 399; Steiner, *Diss. Erlangen*, 1897; Plinke, *Diss. Jena*, 1898). Unlike glycollamide, which is not an electrolyte, glycolliminohydrin has a conductivity in aqueous solution corresponding with that of the salts; $\mu_{64} = 67{\cdot}30$; $\mu_{2048} = 79{\cdot}50$; $\Delta^{2040-64} = 12{\cdot}2$. This is due to the dissociation of the molecule $OH{\cdot}CH_2{\cdot}C({:}NH){\cdot}O{\cdot}NH_2{:}C(OH){\cdot}CH_2{\cdot}OH$, which is of the ammonium type, into the ions $OH{\cdot}CH_2{\cdot}C({:}NH){\cdot}O{\cdot}$ and $OH{\cdot}CH_2{\cdot}C(OH){:}NH_2{\cdot}$; in presence of sodium hydroxide, the conductivity rapidly and continuously falls, owing to the decomposition of the original double molecule into sodium glycollate and ammonia. The initial value of the conductivity points to the formation of the salt $OH{\cdot}CH_2{\cdot}C(ONa){:}NH$, and it is this which then undergoes decomposition; with glycollamide, on the contrary, no such initial salt formation occurs, and the decomposition into sodium glycollate and ammonia is much slower. The depression of the conductivity of a solution of hydrochloric acid by the iminohydrin shows that the formation of the hydrochloride $OH{\cdot}CH_2{\cdot}C(OH){:}NH_2Cl$ in solution is incomplete, but the salt can be easily isolated by evaporation; hydrochloric acid causes little decomposition into glycollic acid and ammonia. The true amides, such as glycollamide, acetamide, dimethylacetamide, carbamide, methylcarbamide, tetramethylcarbamide and benzenesulphonamide cause little depression of the conductivity of hydrochloric acid at a dilution v_{32}, and hence do not give rise to salts of the iminohydrin type, $OH{\cdot}CR{:}NH_2Cl$.

Whereas glycollamide yields, with acetic anhydride, an *acetyl* derivative, $C_2H_4AcO_2N$, melting at 92°, glycolliminohydrin gives principally a non-crystallisable syrup along with a small quantity of a white, amorphous substance which does not melt at 252°. Glycollamide gives, with bromine in alkaline solution, a *bromoamide*, but glycolliminohydrin gives no definite product. Attempts to obtain the iminohydrin from glycollide and ammonia failed; that the former is not an ammonium salt of the type  $ONH_4{\cdot}C{<}{}^{O\cdot CH}_{CH\cdot O}{>}C{\cdot}ONH_4$ is also shown by the fact that in aqueous solution it does not give the Nessler reaction.

[With Max Buchner.]—Fifteen representative amides of carboxylic and sulphonic acids were found to be neutral in reaction and nearly non-conducting in solution; this was the case even with those containing strongly negative groups, such as the sulphonamides of tribromobenzene and the nitrobenzenes. From the conductivity of the carboxylic amides in sodium hydroxide solution, it appears that they do not give rise to salts in solution; the sodium salts of the sulphonamides exist, however, in solution although more or less hydrolysed, even in the case of tribromo- and dinitro-benzenesulphonamides. Benzenesulphobenzamide, $PhSO_2{\cdot}NHBz$, on the contrary, is a weak acid and yields a sodium salt, the conductivity of which shows it to be neutral. Acid imides such as phthalimide are very sensitive to sodium hydroxide, and are converted into sodium salts of amino-acids. "Saccharin" is, however, not only a strong and stable acid ($K = 0{\cdot}387$) yielding stable neutral salts, but is stronger than either *o*- or *p*-sulphaminobenzoic acid ($K = 0{\cdot}206$ and $0{\cdot}025$ respectively).

Attempts to prepare iminoethers of the type $C_6H_5{\cdot}SO(OR){:}NH$ by the action of alkyl iodides on the silver derivative of benzenesulphonamide gave only the alkyl derivatives $C_6H_5{\cdot}R{\cdot}SO_2{\cdot}NHR$; the decomposition of the silver or sodium salts of the amides and sulphonamides by hydrogen chloride, cyanide, or sulphide, in absence of water below 0°, gave only the original amides, and not the *iso*-form. The additive compound of benzamide and sodium ethoxide, instead of giving alcohol and the sodium salt, $ONa{\cdot}CPh{:}NH$, when heated, underwent complete decomposition. W. A. D.

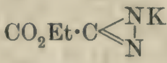
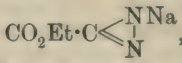
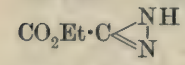
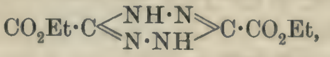
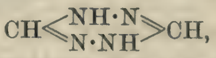
Spontaneous Conversion of Uric Acid into Carbamide. By Torquato Gigli (*Chem. Zeit.*, 1901, **25**, 741).—When dilute solutions of potassium urate are kept for some 2 to 3 years, the urate becomes completely transformed into carbamide and potassium carbonate, probably in accordance with the equation $C_5H_2O_3N_4K + 3H_2O + O_2 = 2CH_4ON_2 + K_2CO_3 + 2CO_2$. J. J. S.

Formation of Berlin Blue and Ferric Hydroxide by the Action of Sunlight on Aqueous Solutions of Potassium Ferricyanide. By J. Matuschek (*Chem. Zeit.*, 1901, **25**, 742—743. Compare this vol., i, 455, 635, 636).—The amounts of ferric hydroxide and of Berlin blue formed depend on the intensity of the illumination and the corresponding differences in temperature. The amounts of Berlin blue form a diminishing arithmetical series when the concentrations of the ferricyanide solutions also form a diminishing arithmetical series. There is always more Berlin blue than ferric hydroxide produced. J. J. S.

Action of Carbon Dioxide on Aqueous Solutions of Ferro- and Ferri-cyanides. By J. Matuschek (*Chem. Zeit.*, 1901, **25**, 815). —Carbon dioxide was passed through boiling solutions containing respectively 1 gram of potassium ferrocyanide and 0·7797 gram of potassium ferricyanide in 100 grams of water. The decomposition was complete after 4 days, and in both cases the products were ferric hydroxide, potassium carbonate, and hydrogen cyanide or its decomposition products, ammonia and formic acid. J. J. S.

Thiocyanogen, the so-called ψ-Thiocyanogen, and the Yellow Colouring Matter obtained from Thiocyanates. By Alwin Goldberg (*J. pr. Chem.*, 1901, [ii], **64**, 166—181. Compare this vol., i, 516).—By the action of hydrogen peroxide or potassium or ammonium persulphate on potassium or ammonium thiocyanate, small quantities of ψ-thiocyanogen are formed. By solution of ψ-thiocyanogen in sulphuric acid and reprecipitation with water, a product is obtained free from oxygen, but still giving all the colour reactions of the original ψ-thiocyanogen, and capable of yielding canarin (*loc. cit.*).

K. J. P. O.

Derivatives of *iso*Diazomethane. By ARTHUR HANTZSCH and MARTIN LEHMANN (*Ber.*, 1901, **34**, 2506—2523).—When a solution of potassium (1 atom.) in ether containing alcohol (2 mols.), or a suspension of sodium ethoxide in ether, is treated at 0° with ethyl diazoacetate, $CO_2Et\cdot CH<\overset{N}{\underset{N}{\|}}$, amorphous yellow *ethyl potassio-* and *sodio-*iso*diazoacetate*,  $CO_2Et\cdot C<\overset{NK}{\underset{N}{|}}$, and  $CO_2Et\cdot C<\overset{NNa}{\underset{N}{|}}$, $\frac{1}{2}H_2O$ are formed respectively. These salts soon decompose spontaneously, even in the dry state; they reduce silver nitrate, mercurous nitrate, and mercuric chloride. When treated with an acid, they yield *ethyl* iso*diazoacetate*,  $CO_2Et\cdot C<\overset{NH}{\underset{N}{|}}$; this is an oil which does not dissolve in water, decomposes when distilled, and polymerises when kept to a glassy, brown deliquescent mass that doubtless consists mainly of ethyl bis*iso*diazoacetate,  $CO_2Et\cdot C<\genfrac{}{}{0pt}{}{NH\cdot N}{N\cdot NH}>C\cdot CO_2Et$, for it yields dihydrotetrazine (bis*iso*diazomethane),  $CH<\genfrac{}{}{0pt}{}{NH\cdot N}{N\cdot NH}>CH$, on prolonged boiling with water. When ethyl *iso*diazoacetate is treated with hydrochloric acid (as, for instance, when a solution of one of the salts in dilute hydrochloric acid is concentrated on the water-bath), it is decomposed into hydrazine and oxalic acid. Unlike the diazoacetate, it does not form an additive product with sulphites. A solution of an alkali salt in water decomposes spontaneously, alcohol then precipitates a mixture of potassium carbonate and bisdiazoacetate with some bisazoxyacetate. When an aqueous solution of the sodium salt is distilled, *iso*diazomethane is not obtained, as might be hoped, neither is Curtius's "third isomeride" of similar composition (Abstr., 1889, 371) formed. This substance does not exist; a mixture of hydrocyanic acid and ammonia is really obtained, doubtless from the decomposition of *iso*diazomethane formed as the immediate product

$$(3CH{:}N_2H = 3HCN + NH_3 + N_2),$$

and this mixture was mistaken for a single, new substance. Nor is such a substance formed when an alkali diazoacetate is distilled with water, provided that the salt be pure. But when ethyl diazoacetate is boiled with an aqueous alkali and the product distilled, although the main product is a bisdiazoacetate, yet the distillate contains hydrocyanic acid and ammonia, so that a certain amount of isomerisation (into *iso*diazoacetate) must have taken place.

A convenient way of preparing potassium diazoacetate, $CO_2K\cdot CH{:}N_2$, is described. Ethyl diazoacetate (1 mol.) is shaken with 15 per cent. aqueous potassium hydroxide (1 mol.) until solution has been effected, and then alcohol and ether are added; an oil separates from which yellow needles crystallise when it is allowed to remain. Warming with strong aqueous potassium hydroxide polymerises this salt to the bisdiazoacetate, $CO_2K\cdot CH{:}N_4{:}CH\cdot CO_2K$. In the same way, diazomethane, $CH_2{:}N_2$, polymerises in ethereal solution to bisdiazomethane, $CH_2\cdot N_4\cdot CH_2$, when exposed to sunlight.

C. F. B.

Mixed Organomagnesium Compounds and their Application to the Synthesis of Acids, Alcohols, and Hydrocarbons. By VICTOR GRIGNARD (*Chem. Centr.*, 1901, ii, 622—625; from *Ann. Univ. Lyon*, 1901, No. 6, 1—116. Compare Abstr., 1900, i, 382, and this vol., i, 250, 263, 316, and 393).—The organomagnesium compounds, $RMgI$ and $RMgBr$, prepared by the action of magnesium on the alkyl haloids in ether, contain ether of crystallisation which may be removed by prolonged heating at 150° in a vacuum. Magnesium methiodide decomposes at 255° and magnesium ethobromide at 200—300°, forming ethane and ethylene. When carbon dioxide is passed into an ethereal solution of an organomagnesium compound and the precipitate, $R\cdot CO_2\cdot MgX$, decomposed by ice and dilute sulphuric acid, the corresponding acid is formed. Acetic, *iso*valeric, and *iso*hexoic acids have been prepared by this method. By the action of magnesium methiodide on acetaldehyde, *iso*propyl alcohol is obtained. Di*iso*butylcarbinol, from *iso*valeraldehyde and magnesium *iso*butylbromide, boils at 113—115° under 87 mm. pressure, has the sp. gr. 0·8237 at 0°, 0·8155 at 12°/4° and n_D 1·42629 at 12°. The *acetate* has a fruity odour and boils at 122—123° under 88 and at 183° under 750 mm. pressure. *Δ^{β}-pentene-δ-ol*, $CHMe\colon CH\cdot CHMe\cdot OH$, from crotonaldehyde and magnesium methiodide, boils at 79—80° under 150, at 120—122° under 735 mm. pressure, has the sp. gr. 0·8506 at 0°, 0·8428 at 9·4°/4°, and n_D 1·43362 at 9·4°. The *acetate* boils at 136—137° under 751 mm. pressure. *γ-Methyl-Δ^{γ}-hexene-β-ol*, $OH\cdot CHMe\cdot CMe\colon CH\cdot CH_2Me$, from methylethylacraldehyde and magnesium methiodide, boils at 89° under 55 mm. pressure, has the sp. gr. 0·8768 at 0°, 0·8678 at 9·5°/4°, and n_D 1·44874 at 9·5°. The *acetate* boils at 95—97° under 50 mm. pressure. *β-Methyl-Δ^{ζ}-hexene-ε-ol*,

$$CHMe_2\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot CH\colon CHMe,$$

from crotonaldehyde and magnesium *iso*amylbromide, boils at 89—91° under 11 mm. pressure, has the sp. gr. 0·8600 at 0°, 0·8539 at 9°/4°, and n_D 1·44713 at 9°. The *acetate* boils at 96—98° under 13 mm. pressure. *βζ-Dimethyl-Δ^{β}-decene-θ-ol*,

$$CMe_2\colon CH\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH(OH)\cdot CH_2Me,$$

from citronellal and magnesium ethobromide, has a pleasant odour of lemons, boils at 113—116° under 8 mm. pressure, has the sp. gr. 0·8740 at 0°, 0·8655 at 12·3°/4°, and n_D 1·46123. The *acetate* boils at 120—123° under 8 mm. pressure.

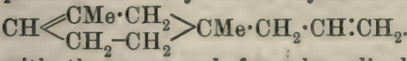
Phenylmethylcarbinol and phenylethylcarbinol have been prepared by the action of benzaldehyde on magnesium methiodide and magnesium ethobromide respectively. *Phenylpropylcarbinol*, $CHPr^{\alpha}Ph\cdot OH$, from benzaldehyde and magnesium propylbromide, boils at 113—115° under 10 mm. pressure, has the sp. gr. 0·997 at 0°, 0·9861 at 13·7°/4°, and n_D 1·51914 at 13·7°. The *acetate* boils at 117—118° under 8 mm. pressure. *Phenyl*iso*propylcarbinol*, from benzaldehyde and magnesium *iso*propylbromide, boils at 112—113° under 15 mm. pressure, has the sp. gr. 0·9986 at 0°, 0·9869 at 13·7°/4°, and n_D 1·51932 at 13·7°. The *acetate* boils at 122—125° under 20 mm. pressure. Phenyl*iso*butylcarbinol has the sp. gr. 0·9726 at 0°, 0·9597 at 17·6°/4° and n_D 1·50798 at 17·6°. The *acetate* boils at 125—126° under 9 mm. pressure. *Phenyl*iso*amylcarbinol*, $OH\cdot CHPh\cdot CH_2\cdot CH_2\cdot CHMe_2$, from benzaldehyde and magnesium *iso*amylbromide, boils at 132° under 8 mm. pressure, has the sp. gr. 0·9674 at 0°, 0·9536 at 18·5°/4° and n_D 1·50714 at 18·5°. The *acetate*, boils at 137—139° under 9 mm. pressure. *2-Furfuryl*iso*amylcarbinol*, $C_4OH_3 \cdot CH(OH) \cdot CH_2 \cdot CH_2Pr^\beta$, from furfuraldehyde and magnesium *iso*amylbromide, has a faint odour which does not resemble that of furfuraldehyde, boils at 110° under 8 mm., at 118° under 14 mm. pressure, has the sp. gr. 0·9998 at 0°, 0·9882 at 12°/4°, and n_D 1·47939 at 12°. The *acetate* has a penetrating odour and quickly becomes yellow; it boils at 123—124° under 14 mm. pressure. By the action of magnesium benzylbromide on aldehydes, only dibenzyl is formed.

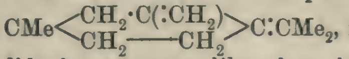
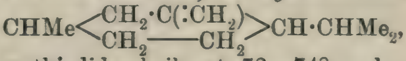
By the action of acetone on magnesium methiodide and magnesium *tert.*butyliodide respectively, trimethylcarbinol and pentamethylethanol, $CMe_3 \cdot CMe_2 \cdot OH$, are obtained, the last, however, only in very small quantity and in the form of the hydrate. Dimethyl*iso*amylcarbinol, $OH \cdot CMe_2 \cdot CH_2 \cdot CH_2Pr^\beta$, from acetone and magnesium *iso*amylbromide, boils at 150—153° under 756 mm. pressure, has the sp. gr. 0·8203 at 0°, 0·8115 at 11·4°/4°, and n_D 1·42428 at 11·4°. The *acetate* has an odour like that of cedar wood, and boils at 171—173° under 745 mm. pressure. *Phenyldimethylcarbinol* crystallises in small prisms, melts at 23°, and boils at 91° under 8 mm. pressure. *Benzyldimethylcarbinol* melts at 0°, has the sp. gr. 0·9960 at 0°, 0·9822 at 13·7°/4°, and n_D 1·51950 at 13·7°. *a-Naphthyldimethylcarbinol* boils at 159—161° under 9 mm. pressure and is easily soluble in ether, methyl alcohol, alcohol, benzene, or ethyl acetate, and slightly so in light petroleum.

By the action of organomagnesium compounds on the esters of monobasic acids, tertiary alcohols are formed except in the cases of the esters of formic acid which yield secondary alcohols. Diethylcarbinol, $CHEt_2 \cdot OH$, from ethyl formate and magnesium ethylbromide, boils at 114—115° under 749 mm. pressure, has the sp. gr. 0·8391 at 0°, 0·8271 at 14·7°/4°, and n_D 1·41243. *Di*ïso*amylcarbinol* has the sp. gr. 0·840 at 0°, 0·8305 at 12·6°/4°, and n_D 1·43801 at 12·6°. *Methyldi*ïso*amylcarbinol* has the sp. gr. 0·847 at 0°, 0·8373 at 12·3°/4°, and n_D 1·44253. The *acetate* boils at 120° under 16 mm. pressure, has the sp. gr. 0·864 at 16·9°/4°, and n_D 1·43191 at 16·9°. Phenyldimethylcarbinol is formed by the action of magnesium methiodide on methyl benzoate.

In many of the preceding reactions, hydrocarbons are formed by the elimination of water from the alcohols and in some cases they constitute the main products. The following hydrocarbons have been prepared in this way or by the action of acetic anhydride on the corresponding alcohols. *βδ-Dimethyl-$\Delta^{\beta\delta}$-pentadiene*, has the sp. gr. 0·7595 at 0°, 0·7490 at 12°/4°, and n_D 1·44684 at 12°. The *tetrabromide* is a stable liquid. The *dihydrobromide* boils at 83—84° under 7 mm. pressure. By the action of an 80 per cent. solution of sulphuric acid on the hydrocarbon, it forms the dimeric *compound*, $(C_7H_{12})_2$, which boils at 98—100° under 12 mm. pressure, has the sp. gr. 0·8869 at 0°, 0·8706 at 10°/4°, and n_D 1·48483 at 10°. *βζ-Dimethyl-$\Delta^{\delta\zeta}$-heptadiene*, $CHMe_2 \cdot CH_2 \cdot CH{:}CH \cdot CMe{:}CH_2$, from synthetical methylheptenone and magnesium methodide, boils at 143—145° under 755 mm. pressure, has a sp. gr. 0·7648 at 10°/4°, and n_D 1·46202 at 10°. The *dihydrobromide* boils at 110—112° under 10 mm. pressure with slight decomposition. *βζ-Dimethyl-$\Delta^{\beta\zeta\theta}$-nonatriene,*

$CMe_2\colon CH\cdot CH_2\cdot CH_2\cdot CMe\colon CH\cdot CH\colon CH_2$,

from citral and magnesium methiodide, has a pleasant odour of lemons, boils and decomposes at 195—197° under 750 mm., and boils at 76—78° under 8 mm. pressure; it has the sp. gr. 0·8215 at 0°, 0·814 at 11·3°/4° and n_D 1·48686 at 11·3°. By the action of hydrogen bromide, it forms two or more isomeric trihydrobromides which are partly solid and partly liquid and when treated with an 80 per cent. solution of sulphuric acid it yields a hydrocarbon, probably of the composition  $CH{<}\begin{matrix}CMe\cdot CH_2\\ CH_2-CH_2\end{matrix}{>}CMe\cdot CH_2\cdot CH\colon CH_2$. This hydrocarbon is identical with that prepared from homolinalool by Tiemann (Abstr., 1896, i, 271); it has an odour like that of terpene, boils at 67—69° under 9 mm., and at 183—185° under 741 mm. pressure, has the sp. gr. 0·8525 at 0°, 0·8450 at 9·9°/4°, and n_D 1·47281 at 9·9°. The *dihydrobromide* boils at 130—135° under 10 mm. pressure.

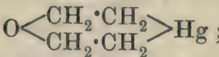
The *terpene*,  $CMe{<}\begin{matrix}CH_2\cdot C(\colon CH_2)\\ CH_2 \text{———} CH_2\end{matrix}{>}C\colon CMe_2$, from pulegone and magnesium methiodide, has a terpene-like odour, boils at 64—65° under 9 mm., and at 177—179° under 744 mm. pressure, has the sp. gr. 0·8518 at 0°, 0·8479 at 8·9°/4°, and n_D 1·47860 at 8·9°. By the action of bromine, it forms a mixture of dibromide and tetrabromide; the *hydrobromide* is a liquid. *3-Methenementhane*,  $CHMe{<}\begin{matrix}CH_2\cdot C(\colon CH_2)\\ CH_2 \text{———} CH_2\end{matrix}{>}CH\cdot CHMe_2$, from menthone and magnesium methiodide, boils at 72—74° under 10 mm. pressure, has the sp. gr. 0·8452 at 0°, 0·8371 at 10·6°/4°, and n_D 1·46510 at 10·6°. *βεθ-Trimethyl-Δ^{ϵ}-nonene,*

$CHMe_2\cdot CH_2\cdot CH_2\cdot CMe\colon CH\cdot CH_2\cdot CHMe_2$,

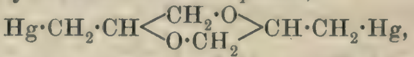
from methyldi*iso*amylcarbinol, acetic anhydride, and sodium acetate, boils at 74—76° under 9 mm. pressure, has the sp. gr. 0·7768 at 0°, 0·7678 at 12·3°/4°, and n_D 1·43521 at 12·3°. Phenylmethylethylene, $CMePh\colon CH_2$, prepared by the action of acetic anhydride on phenyldimethylcarbinol, boils at 106° under 126 mm., and at 158—160° under 748 mm. pressure, has a sp. gr. 0·9165 at 9·6°/4°, and n_D 1·54207 at 9·6°. The *dibromide* boils and decomposes at 111—114° under 7 mm. pressure. When the hydrocarbon is heated with concentrated hydrochloric acid under pressure, it polymerises, forming the *hydrocarbon* $C_{18}H_{20}$, which crystallises in triclinic prisms, melts at 52—53°, and boils at 158—159° under 8 mm. pressure. *α-Phenyl-β-methyl-Δ^{α}-propylene,* $CHPh\colon CMe_2$, prepared from benzyldimethylcarbinol, boils at 76—77° under 11 mm., and at 183—185° under 748 mm. pressure, has a sp. gr. 0·9298 at 0°, and yields a liquid *dibromide*. *α-Phenyl-γ-methyl-$\Delta^{\alpha\gamma}$-tetradiene*, $CHPh\colon CH\cdot CMe\colon CH_2$, prepared by the action of acetic anhydride on the product obtained from benzylideneacetone and magnesium methiodide, forms crystals, melts at 27°, boils at 115° under 18 mm. pressure, and polymerises readily. The composition of the hydrocarbon formed by the action of magnesium *iso*amylbromide on β-naphthyl methyl ketone is doubtful, but may possibly be

$CH_2\colon C(C_{10}H_7)\cdot CH_2\cdot CH_2\cdot CHMe_2$ or $C_{10}H_7\cdot CMe\colon CH\cdot CH_2\cdot CHMe_2$.

The organomagnesium compounds are more generally applicable, more convenient to handle, and give better yields in the synthesis of monobasic acids, alcohols, and hydrocarbons than the organozinc compounds. E. W. W.

Cyclic Mercury-Carbon Compounds. By JULIUS SAND (*Ber.*, 1901, **34**, 2910—2915).—When ethyl ether mercuric bromide (Abstr., 1900, i, 618) is reduced with alkaline stannite solution, it yields *mercurodiethylene oxide*, $O\colon(C_2H_4)_2\colon Hg_2$, in the form of a bluish-black precipitate which sinters at 80° and melts between 140° and 150°; it is insoluble in water, alkalis, and the usual organic solvents, is completely decomposed by hot hydrochloric acid, and when heated with benzene at 140° is converted into mercury and *mercuridiethylene oxide*,  $O<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>Hg$; this crystallises in glistening, colourless needles with a characteristic odour, melts at 145°, and is insoluble in water, alkalis, and dilute mineral acids, but is readily soluble in most organic solvents with the exception of ether and acetone. It is not decomposed when heated with potassium hydroxide, iodide, or cyanide; but with fuming hydrochloric acid gives a theoretical yield of ethylene. It forms a *mercurichloride*, $C_4H_8OHg,2HgCl_2$, and also a complex *picrate* decomposing at 80°.

Dipropylene oxide mercuric bromide (this vol., i, 458) and alkaline stannite solution yield a brick-red *compound*,



$$Hg\cdot CH_2\cdot CH<\begin{matrix}CH_2\cdot O\\O\cdot CH_2\end{matrix}>CH\cdot CH_2\cdot Hg,$$

which turns brown on exposure to light, and after ten hours' exposure and subsequent extraction with benzene, yields a *mercuri*-compound, $C_6H_{10}O_2Hg$, which melts at about 190°, is insoluble in water, alkalis, dilute acids, or acetone, but readily soluble in benzene or toluene, is decomposed by concentrated hydrochloric acid, and gives precipitates with mercuric chloride and picric acid. J. J. S.

Acetylacetone Compounds of Platinum. By ALFRED WERNER (*Ber.*, 1901, **34**, 2584—2593).—When potassium platinochloride, K_2PtCl_4, is heated with about 10 times its weight of 10 per cent. aqueous potassium hydroxide until the liquid has acquired a yellowish shade, shaken with twice its weight of acetylacetone, and the heating and shaking continued for a time, a bright yellow, crystalline powder separates. By further treatment with a little strong potash and acetylacetone, the mother liquor can be made to yield more crystals; this treatment can be repeated several times. The substance in question is *platinum acetylacetonate*, PtA_2, where A is $\cdot O\cdot CMe\colon CH\cdot CMeO$ or $\cdot CH(CMeO)_2$, according as the substance is regarded as derived from the enolic or the ketonic form of acetylacetone. It is not decomposed by strong mineral acids, and does not give a coloration with ferric chloride. It raises the boiling point of chloroform by an amount corresponding with that required by the formula given.

When a 25 per cent. solution of potassium platinochloride is heated to boiling, shaken with half its weight of acetylacetone and one-fourth its weight of 25 per cent. aqueous potassium hydroxide, and shaken again after 10 minutes with as much more potash, orange-yellow crystals separate, followed after a time by bright yellow crystals. The first *salt*, KCl,PtClA, gives no red coloration with ferric chloride, or precipitate with salts of heavy metals; from its solution in water it can be salted out by potassium chloride or potassium hydroxide, but it is not precipitated by hydrochloric acid. The second *salt*, KA,PtClA, gives a brownish-red coloration with ferric chloride in dilute solution, and a brown precipitate in strong solution; it gives precipitates also with the salts of other heavy metals. When shaken with methyl sulphate and aqueous potassium hydroxide, it yields an oil which crystallises eventually, and is presumably a methyl derivative. When its aqueous solution is mixed with hydrochloric acid, a yellow, amorphous *substance*, HA,PtClA, is precipitated. This is soluble in organic solvents; alkalis also dissolve it, and it is reprecipitated in the crystalline form from these solutions by hydrochloric acid. When freshly precipitated, it dissolves in water, but is reprecipitated from this solution by hydrochloric acid. After it has been kept, it dissolves to a smaller extent in water, but the solution is no longer precipitated by hydrochloric acid; probably a transformation of the HA group from the enolic to the ketonic form has taken place. When a solution of it in ammonia is mixed with rubidium chloride, a yellow, crystalline *salt*, RbA,PtClA, is precipitated.

When a hot 25 per cent. solution of potassium platinochloride is mixed with about half its weight of acetylacetone and half its weight of 33 per cent. aqueous sodium hydroxide, a golden-yellow *salt*, $NaCl,PtClA,NaA,5H_2O$, is precipitated; this gives at once a deep red coloration with ferric chloride, and precipitates with the salts of heavy metals. When a strong aqueous solution of it is boiled until the colour has become dark, but not quite black, and then saturated with sodium chloride, a yellow *salt* is precipitated which can be crystallised from chloroform; it is then greenish-yellow in colour, and has the composition $NaA,PtClA,2H_2O,CHCl_3$. This salt is a derivative of the substance, HA,PtClA, described above, for this substance is precipitated when a solution of the salt is mixed with hydrochloric acid.

C. F. B.

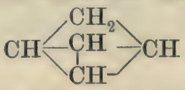
Hexamethylene [*cyclo*Hexane]. By Nicolai D. Zelinsky (*Ber.*, 1901, **34**, 2799—2803. Compare Abstr., 1895, i, 411).—*cyclo*Hexane, prepared by Baeyer's method, melts at 2°, boils at 80·8—81° (corr.), has a sp. gr. 0·7763 at 20°/4°, and the refractive index n_D 1·4269 at 18° (compare *loc. cit.*). The crystals belong to the regular system and act very feebly on polarised light. *cyclo*Hexanone, prepared from pimelic acid, boils at 155·4° (corr.), and has a sp. gr. 0·9467 at 19°/4° and n_D 1·4503 at 19°. The *cyclo*hexanol, obtained from the ketone, boils at 160·9° (corr.), has a sp. gr. 0·9471 at 22°/4°, and n_D 1·4650 at 22°.

In the reduction of *cyclo*hexanone with sodium, *cyclo*hexanol is formed together with cyclo*hexanepinacone*, $C_{12}H_{22}O_2$, which crystallises in small, white needles melting at 129—130°.

When *cyclo*hexane is prepared by reduction of *cyclo*hexanyl iodide by zinc dust in the presence of dilute alcohol (compare Abstr., 1899, i, 181), it melts at 6·4°, boils at 80·8—80·9° (corr.), has a sp. gr. 0·7788 at 19·5°/4°, and n_D 1·4266 at 19·5°. These constants closely approximate to those found for *cyclo*hexane obtained by Young and Fortey (Trans., 1899, **75**, 880) from naphtha, and for hexamethylene, prepared by Sabatier and Senderens (this vol., i, 263, 459) by reduction of benzene.

On heating *cyclo*hexane under pressure with excess of bromine at 150—200° for several days, 1 : 2 : 4 : 5-tetrabromobenzene (m. p. 177—178°) is formed. K. J. P. O.

Oxidation of Homologues of Benzene. By EYVIND BOEDTKER (*Bull. Soc. Chim.*, 1901, [iii], **25**, 843—852).—The oxidation of cumene (*iso*propylbenzene) by chromic acid in acetic acid solution gives rise to the formation of about 10 per cent. of *phenyldimethylcarbinol*, $CMe_2Ph\cdot OH$, a colourless, highly refracting liquid of strong aromatic odour, which boils and partially decomposes at 215—220°, does not solidify at $-18°$, has a sp. gr. 1·0177 at 20°, and n_D 1·5314 at 18·5°.

According to Mensel, cumene, when treated with bromine, yields *o*-bromocumene and a solid substance which is now shown to be a hydrocarbon, $C_{17}H_{14}$, to which the name 3 : 5-*diphenyl*isocyclo*pentenine* and the constitution  are assigned; it crystallises in white scales melting at 211° (corr.), distils above 300°, is not acted on by the halogens or by chromic acid, and is insoluble in alcohol but more or less soluble in other organic solvents.

The oxidation of toluene by chromic acid in acetic acid solution leads to the production of benzyl alcohol, benzyl acetate, dibenzyl, and other compounds which were not identified. N. L.

Replacement of Oxygen by Fluorine in the Iodoxy-compounds. By RUDOLPH F. WEINLAND and W. STILLE (*Ber.*, 1901, **34**, 2631—2633. Compare Abstr., 1899, ii, 363).—Iodoxy-compounds are converted by concentrated hydrofluoric acid into iodosofluorides, one atom of oxygen being displaced by two atoms of fluorine. The crystals are stable in dry air, but are decomposed by moist air and by water. When heated, they decompose explosively. *Benzene iodosofluoride*, $IPhOF_2$, crystallises in lustrous, matted needles and decomposes at 216°. o-*Tolueneiodosofluoride*, $C_6H_4Me\cdot IOF_2$, crystallises in leafy aggregates of granules; it commences to melt at 120°, and decomposes at 170—190°. p-*Tolueneiodosofluoride*, crystallises in lustrous needles and decomposes at 206°. A. H.

Electrolytic Reduction of Nitro-compounds to Amines. C. F. BOEHRINGER & SONS (D.R.-P. 117007).—Nitrobenzene (4 parts) mixed in the cathode cell with 16 parts of concentrated hydrochloric acid diluted with its own weight of water, is quantitatively converted into aniline, when cuprous chloride (1 part) is added, and the reduction carried out by an electric current, having a density of 1900 amperes per sq. m., the electrodes being of platinum or other refractory material, and the anode cell containing 10 per cent. sulphuric acid. Similar results are obtained by adding iron, chromium, lead, and mercury salts, or the corresponding metals in a finely divided con-

dition. (Compare D.R.-P. 116942, and this vol., i, 587). Finely divided tin or a tin salt may be placed in the anode cell (Eng. Pat. 4175 of 1900).
G. T. M.

Electrolytic Oxidation of Nitrotoluenes. By P. PIERRON (*Bull. Soc. Chim.*, 1901, [iii], **25**, 852—854).—It has been shown by Elbs (Abstr., 1897, i, 332) that *p*-nitrotoluene yields *p*-nitrobenzyl alcohol when oxidised electrolytically, and it is now shown that *o*- and *m*-nitrotoluene, when similarly treated, yield principally *o*-nitrobenzyl alcohol and *m*-nitrobenzaldehyde respectively. The nitrotoluene is dissolved in a mixture of acetic and sulphuric acids and the liquid electrolysed at 90° between a platinum anode and a nickel cathode, using a current of 1 ampere.
N. L.

Phenyldinitromethane [ω-Dinitrotoluene]. By GIACOMO PONZIO (*Gazzetta*, 1901, **31**, ii, 133—138).—The author has succeeded in preparing this compound by starting from benzyl methyl ketone, which, by the action of sodium ethoxide and amyl nitrite, is converted into *iso*nitrosobenzyl methyl ketone; to the latter compound, suspended in anhydrous ether cooled in ice, the calculated quantity of nitrogen peroxide, previously distilled over phosphoric oxide, is then added. *ω-Dinitrotoluene*, $CHPh(NO_2)_2$, crystallises from ether in large, white prisms melting at 79°. It is soluble in the cold, in organic solvents with the exception of light petroleum, and in hot water, and, with the formation of a yellow coloration, in alkali solutions, but resists the action of dilute acids. It is volatile in a current of steam and gives the normal molecular weight in boiling ether or freezing acetic acid. When heated above 130°, it is decomposed violently, yielding red vapours and benzaldehyde. It dissolves without apparent change in concentrated sulphuric acid, but on heating the solution red vapours are evolved and benzoic acid formed. With phenol and sulphuric acid, it gives no coloration in the cold, but on heating gently the liquid assumes an intense emerald green colour which changes to red on adding water. When reduced, either with glacial acetic acid and zinc dust at a low temperature, or with stannous chloride, it yields benzaldehyde. It does not react with acetic anhydride, acetyl chloride, or phosphorus tri- or penta-chloride. The *potassium* derivative, $CPhK(NO_2)_2$, obtained by the action of alcoholic potassium hydroxide, is precipitated in the form of sparkling, yellow laminæ which are very soluble in water and slightly so in alcohol and when heated explode; when reduced with sodium amalgam or with stannous chloride in presence of sodium carbonate and potassium sodium tartrate, it yields benzaldehyde and ammonia. The *silver* salt, $CPhAg(NO_2)_2$, crystallises from water in brownish-yellow prisms which explode when heated.
T. H. P.

Action of Nitric Acid on *o*-Nitrotoluene-*p*-sulphonamide. Nitration of *p*-Toluenesulphonic Chloride. By FRÉDÉRIC REVERDIN and PIERRE CRÉPIEUX (*Ber.*, 1901, **34**, 2992—2996).—*o*-Nitrotoluene-*p*-sulphonamide, when treated with fuming nitric acid, gives rise to two mononitrotoluenesulphonic acids and a dinitrotoluenesulphonic acid;

the acid seems to have a hydrolytic action, adding the elements of water to the sulphonamide with the formation of an ammonium salt; the production of isomeric mononitro-derivatives points to a simultaneous wandering of the nitro-group.

o-Nitrotoluene-*p*-sulphonic acid is isolated from the products of nitration in the form of its *aniline* and *ammonium* salts, these compounds crystallising from water or alcohol in colourless needles melting respectively at 225° and 221°. The isomeric *ammonium nitrotoluenesulphonate*, obtained from the mother liquors of the preceding ammonium compound, melts at 290°. *Ammonium dinitrotoluenesulphonate* is a white, crystalline substance which does not melt below 300°. *p*-Toluenesulphonic chloride, when nitrated on the water-bath with a mixture of fuming nitric acid and concentrated sulphuric acid, yields 2 : 6-dinitrotoluene-4-sulphonic acid in almost theoretical yield.

G. T. M.

Derivatives of Toluene-*p*-sulphonic Chloride and *o*-Nitrotoluene-*p*-sulphonic Chloride. By Frédéric Reverdin and Pierre Crépieux (*Ber.*, 1901, **34**, 2996—3004).

—Toluene-*p*-sulphonic chloride and its nitro-derivative, when condensed with the phenols in the presence of sodium carbonate, readily yield esters of toluene-*p*-sulphonic acid. The o-*nitrophenyl* ester, $C_6H_4Me\cdot SO_3\cdot C_6H_4\cdot NO_2$, forms colourless crystals melting at 98°; o-*nitrophenyl* o-*nitrotoluene*-p-*sulphonate*, $NO_2\cdot C_6H_4Me\cdot SO_3\cdot C_6H_4\cdot NO_2$, crystallises in colourless needles and melts at 113—114°. These compounds, when reduced, yield bases which, on diazotising and combining with α-naphthol-4-sulphonic acid, give rise to red azo-colouring matters. The *resorcinol* esters, $C_6H_4(SO_3\cdot C_6H_4Me)_2$ and $C_6H_4(SO_3\cdot C_6H_3Me\cdot NO_2)_2$, crystallise in prisms melting respectively at 80—81° and 136°. The latter compound on nitration yields a *mononitro*-derivative crystallising in colourless needles and melting at 105°. The *guaiacyl* ester,

$$C_6H_4Me\cdot SO_3\cdot C_6H_4\cdot OMe,$$

melts at 85° and is readily hydrolysed by concentrated acids or alcoholic potassium hydroxide; it forms a *nitro*-derivative, $C_6H_4Me\cdot SO_3\cdot C_6H_3(NO_2)\cdot OMe$, crystallising in prisms and melting at 145°; the product, when hydrolysed with concentrated sulphuric acid yields 4-nitro-1 : 2-guaiacol. *β-Naphthyl toluene*-p-*sulphonate*,

$$C_6H_4Me\cdot SO_3\cdot C_{10}H_7,$$

crystallises in nacreous leaflets, and melts at 125°; the corresponding *ester*, $C_{10}H_6(SO_3\cdot C_6H_4Me)_2$, from 2 : 7-dihydroxynaphthalene, melts at 150° and is insoluble in alkaline solutions.

The two sulphonic chlorides readily yield substituted amides when condensed with the aromatic amines. The *anilide*,

$$NO_2\cdot C_6H_3Me\cdot SO_2\cdot NHPh,$$

melts at 109°; *toluenesulphone*-2 : 4-*dinitroanilide*,

$$C_6H_4Me\cdot SO_2\cdot NH\cdot C_6H_3(NO_2)_2,$$

produced on nitrating the anilide, melts at 219°; the *nitro*-compound, $NO_2\cdot C_6H_3Me\cdot SO_2\cdot NH\cdot C_6H_3(NO_2)_2$, obtained in a similar manner from the corresponding anilide, melts at 214°.

The *phenylhydrazide*, $NO_2\cdot C_6H_3Me\cdot SO_2\cdot NH\cdot NHPh$, melts at

157—158° ; it yields an amine on reduction, the diazonium salt of which furnishes an azo-compound with α-naphthol-4-sulphonic acid.

The *phenetidide*, $C_6H_4Me\cdot SO_2\cdot NH\cdot C_6H_4\cdot OEt$, crystallises in needles and melts at 106—107°. The *phenylenediamide*,

$$C_6H_4(NH\cdot SO_2\cdot C_6H_4Me\cdot NO_2)_2,$$

obtained from *m*-phenylenediamine, melts above 300° and yields on reduction an amine which gives rise to red azo-compounds.

Bis-toluene-p-*sulphone*-p-*phenylenediamide*, $C_6H_4(NH\cdot SO_2\cdot C_6H_4Me)_2$, melts above 250°.

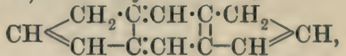
The *naphthalides*, $NO_2\cdot C_6H_3Me\cdot SO_2\cdot NH\cdot C_{10}H_7$, derived from α- and β-naphthylamine, melt at 157° and 161° respectively, and yield on reduction amines forming well crystallised hydrochlorides and giving rise to red azo-colouring matters. G. T. M.

1 : 5-Chloronitronaphthalene from 1-Chloronaphthalene. Chemische Fabrik Griesheim-Elektron (D. R.-P. 120585).—The crude product from the nitration of 1-chloronaphthalene, when treated with alcoholic ammonia at 170—180°, yields a mixture of 4-nitro-α-naphthylamine and unaltered 1 : 5- and 1 : 8-chloronitronaphthalenes. The chloronitronaphthalenes are removed by extraction with carbon tetrachloride or a mixture of carbon disulphide and light petroleum, and the residue left after distilling off the solvent is crystallised from alcohol in order to free the 1 : 5-compound from traces of the 1 : 8-isomeride. G. T. M.

Preparation of 1 : 5-Dinitro- and 1 : 3 : 8-Trinitro-naphthalenes. Kalle & Co. (D. R.-P. 117368).—Nitronaphthalene dissolved in 6 parts of concentrated sulphuric acid, and nitrated with concentrated nitric acid (1 mol.), mixed with 2·5 parts of concentrated sulphuric acid, yields a product from which 1 : 5-dinitronaphthalene (m. p. 211°) separates on cooling; the mother liquor, on further nitration, yields 1 : 3 : 8-trinitronaphthalene (m. p. 218°). The 1 : 8-dinitro-compound partly separates along with its isomeride when a smaller quantity of sulphuric acid is employed. G. T. M.

Preparation of Dinitronaphthalenesulphonic Acids. Farbwerke vorm. Meister, Lucius, & Brüning (D. R.-P. 117268).—Although 1 : 5- and 1 : 8-dinitronaphthalenes are converted by excess of fuming sulphuric acid into nitrosonitronaphthols (Graebe, Abstr., 1900, i, 24 ; Friedländer, *ibid.*, 150), yet, when treated with acid containing very little sulphur trioxide, they yield dinitronaphthalenesulphonic acids. The dinitro-compound, dissolved in 6 parts of ordinary concentrated sulphuric acid, is treated with 2 parts of 20 per cent. fuming acid slowly added, the mixture is then poured into brine solution, when the sodium salt of the monosulphonic acid separates, and may be crystallised from alcohol. The 1 : 5-compound yields 1 : 5-dinitronaphthalene-3-sulphonic acid, of which the *chloride* melts at 118—119° ; the 1 : 8-isomeride gives rise to 1 : 8-dinitronaphthalene-3-sulphonic acid, of which the *chloride* melts at 143—144° (compare D. R.-P. 85058). G. T. M.

Synthesis of Indacene Derivatives. By FRITZ EPHRAIM (*Ber.*, 1901, **34**, 2779—2794).—The hydrocarbon,

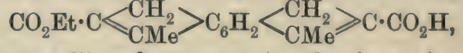


$$CH{<}\begin{array}{l}CH_2\cdot C\colon CH\cdot C\cdot CH_2\\ CH-C\colon CH\cdot C-CH\end{array}{>}CH,$$

is termed indacene, and its tetrahydro-derivative, $C_{12}H_{14}$, hydrindacene. The author has obtained derivatives of indacene and of tetraketohydrindacene by the condensation of ethyl *m*-xylylenediacetoacetate and of ethyl benzene-1 : 2 : 4 : 5-tetracarboxylate with ethyl acetate (compare Wislicenus and Kötzle, Abstr., 1889, 1067, 1068).

The *sodium* salt of ethyl tetraketohydrindacenedicarboxylate, $CO_2Et\cdot CNa{<}\begin{array}{l}CO\\ CO\end{array}{>}C_6H_2{<}\begin{array}{l}CO\\ CO\end{array}{>}CNa\cdot CO_2Et$, is a brick-red powder, and is prepared by adding ethyl acetate slowly to ethyl benzene-1 : 2 : 4 : 5-tetracarboxylate and sodium heated at 100°; the free *ester* is a red powder.

Ethyl m-*xylylenediacetoacetate*, $C_6H_4(CH_2\cdot CHAc\cdot CO_2Et)_2$, prepared from ω-dibromo-*m*-xylene, ethyl acetoacetate, and sodium ethoxide, is a colourless, viscous oil. On treating the ester with 80 per cent. sulphuric acid, *ethyl hydrogen dimethylindacenedicarboxylate*,



$$CO_2Et\cdot C{<}\begin{array}{l}CH_2\\ CMe\end{array}{>}C_6H_2{<}\begin{array}{l}CH_2\\ CMe\end{array}{>}C\cdot CO_2H,$$

is formed, and crystallises from water in colourless, microscopic needles melting at 165—166°; the *silver* salt forms white flakes. *Dimethylindacenedicarboxylic acid*, prepared by hydrolysing the ester by potassium hydroxide, is a brownish-yellow powder melting above 300°. The tetrabromide, *dimethyltetrabromohydrindacenedicarboxylic acid*, $C_{16}H_{14}O_4Br_4$, is prepared by the action of bromine on the acid or its monoethyl ester, and is a white, crystalline powder, which does not melt at 300°.

Dimethylindacene, $C_6H_2\left({<}\begin{array}{l}CH_2\\ CMe\end{array}{>}CH\right)_2$, obtained by distilling dimethylindacenedicarboxylic acid with soda-lime, is a yellowish oil, boiling without decomposition at a high temperature, and has a characteristic odour resembling that of indene; when exposed to the air, it resinifies.

When distilled under reduced pressure or when kept, ethyl *m*-xylylenediacetoacetate is converted into a syrup, which, on treatment with 80 per cent. sulphuric acid, yields a neutral *substance*, $C_{18}H_{18}O_4$; with bromine, this gives a dibromide.

Many fruitless attempts were made to prepare indacene derivatives from *p*-phenylenediacrylic and *p*-phenylenedipropionic acids. *p*-Phenylenediacrylic acid can be directly prepared from terephthalaldehyde by Perkin's reaction (compare Löw, Abstr., 1886, 461). *Methyl*-p-*aldehydocinnamate*, $CHO\cdot C_6H_4\cdot CH\colon CH\cdot CO_2Me$, prepared from *p*-aldehydocinnamic acid, crystallises in white needles melting at 82—83°. *p*-Phenylenetetrabromodipropionic acid, prepared from *p*-phenylenediacrylic acid and bromine, is a white, crystalline powder melting at 251° (compare Löw, *loc. cit.*); its sodium salt decomposes in solution, with the formation of p-*phenylenedibromodiethylene*, $C_6H_4(CH\colon CHBr)_2$, which crystallises in needles melting at 135°.

p-*Xylylenedichloromalonic acid*, $C_6H_4[CH_2\cdot CCl(CO_2H)_2]_2$, prepared from the corresponding ethyl ester, forms crystals which melt and decompose at 179°; the *potassium* salt crystallises in needles. On heating the acid alone or with concentrated sulphuric acid, p-*phenylenedichloropropionic acid*, $C_6H_4(CH_2\cdot CHCl\cdot CO_2H)_2$, is obtained, and forms crystals melting at 165°.

Ethyl p-*xylylenedimethylmalonate*, $C_6H_4[CH_2\cdot CMe(CO_2Et)_2]_2$, prepared from the sodium salt of ethyl *p*-xylylenedimalonate and methyl iodide, crystallises in groups of needles melting at 75°; on hydrolysis of the ester with potassium hydroxide, the *potassium* salt was obtained as long, white needles. From the latter an oily acid (probably *p*-xylylenedimethylmalonic acid) was prepared, which, when heated with water under pressure finally at 175°, yielded p-*phenylenediisobutyric acid*, $C_6H_4(CH_2\cdot CHMe\cdot CO_2H)_2$; this acid forms small, white crystals melting at 169°. K. J. P. O.

Condensation Products of 2:4-Dinitrotoluene. By JOHANNES THIELE and RICHARD ESCALES (*Ber.*, 1901, **34**, 2842—2848).—Dinitrotoluene condenses with benzaldehyde in the presence of piperidine, forming stilbene derivatives. The piperidine can be replaced by other amines, such as diethylamine, triethylamine, or ammonia, but the yields are much smaller. 2 : 4-*Dinitrostilbene*, $C_{14}H_{10}O_4N_2$, separates from acetic acid in bright yellow, compact crystals melting at 139—140°, and forms a *dibromide*, $C_{14}H_{10}O_4N_2Br_2$, which crystallises from xylene in white prisms melting and decomposing at 185—186°. When reduced with stannous chloride and hydrochloric acid in glacial acetic acid solution, it yields 2 : 4-*diaminostilbene*, $C_{14}H_{14}N_2$, which crystallises from benzene in bright yellow, lustrous needles melting at 119—120°, and forms a *dihydrochloride*, which crystallises, with $2H_2O$, in needles.

When 2 : 4-dinitrostilbene is partially reduced under the conditions just described, the compound obtained is probably 4-*nitro*-2-*aminostilbene*, $C_{14}H_{12}O_2N_2$; this separates from alcohol in reddish crystals, melts at 142—143°, and yields a *hydrochloride* which melts at 218—219° and is decomposed by water, and an *acetyl* derivative, $C_{16}H_{14}O_3N_2$, which crystallises in bright yellow, felted needles and melts at 220°. The partial reduction of 2 : 4-dinitrostilbene with ammonium sulphide yields a compound which is probably 2-*nitro*-4-*aminostilbene*; this separates from alcohol in ruby-coloured crystals, melts at 110—111°, and forms a *hydrochloride* which crystallises in golden laminæ melting at 223°, and an *acetyl* derivative which crystallises in flat, orange-coloured plates and melts at 192—193°.

2 : 4 : 4′-*Trinitrostilbene*, $C_{14}H_9O_6N_3$, obtained when *p*-nitrobenzaldehyde is used in the condensation, crystallises from nitrobenzene in lemon-coloured, felted needles and melts at 240°. When reduced with stannous chloride, it yields 2 : 4 : 4′-*triaminostilbene*, $C_{14}H_{15}N_3$, which crystallises from toluene in small, yellow clumps and melts at 176—177°.

2 : 4 : 3′-*Trinitrostilbene*, obtained from *m*-nitrobenzaldehyde, crystallises from acetic acid in yellow, felted needles, melts at 183—184°, and, when reduced, yields 2 : 4 : 3′-*triaminostilbene*, which forms small, yellow crystals melting at 112—113°.

2 : 4 : 2′-*Trinitrostilbene* separates from acetic acid in greenish-yellow

crystals, melts at 194—195°, and, when reduced, yields 2 : 4 : 2′-*triaminostilbene*, which is obtained in lustrous, yellow crystals melting at 156—157°. R. H. P.

Isomeric Diamino-bases of α-Cyanostilbene. By MARTIN FREUND (*Ber.*, 1901, **34**, 3104—3108).—4 : 4′-*Dinitro-α-cyanostilbene*, $NO_2 \cdot C_6H_4 \cdot C(CN) \vdots CH \cdot C_6H_4 \cdot NO_2$, obtained by the nitration of α-cyanostilbene or by the condensation of *p*-nitrobenzyl cyanide and *p*-nitrobenzaldehyde, crystallises in silky, yellow needles, melts at 215°, and when reduced with tin and hydrochloric acid yields the corresponding 4 : 4′-*diamino*-compound, which crystallises in small, reddish-brown needles and melts at 188°.

m-Nitrobenzyl cyanide condenses with *m*-nitrobenzaldehyde, forming 3 : 3′-*nitro-α-cyanostilbene*, which crystallises from glacial acetic acid, melts at 204°, and when reduced yields the corresponding *diamino*-base, which crystallises in yellow needles melting at 145—146°.

2 : 2′-*Nitro-α-cyanostilbene*, obtained by the condensation of the corresponding *o*-compounds, crystallises from glacial acetic acid and melts at 169—171°.

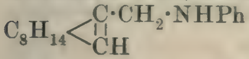
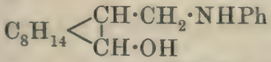
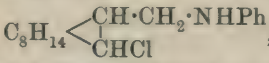
4 : 3′-*Diamino-α-cyanostilbene* crystallises in needles and melts at 108—110° ; the condensation of *p*-nitrobenzyl cyanide and *o*-nitrobenzaldehyde in the presence of sodium ethoxide yields 4 : 2′-dinitro-α-cyanostilbene and 2 : 4′-*dinitro-β-hydroxy-α-cyanodiphenylethane*, $NO_2 \cdot C_6H_4 \cdot CH(OH) \cdot CH(CN) \cdot C_6H_4 \cdot NO_2$, which crystallises from glacial acetic acid and melts at 135—138° ; 4 : 2′-dinitro-α-cyanostilbene, when reduced with tin and hydrochloric acid, yields the *hydrochloride* of 2-amino-3-aminophenylquinoline, which crystallises, with $2H_2O$, in slender, grey needles decomposing at 250°. R. H. P.

Action of Sulphur Monochloride on Anthracene. By EDUARD LIPPMANN and ISIDOR POLLAK (*Ber.*, 1901, **34**, 2767—2769). —On treating anthracene, suspended in petroleum, with a solution of sulphur monochloride, hydrogen chloride is evolved, the anthracene dissolves, and *anthracene dithiochloride*, $C_{14}H_9 \cdot S_2Cl$, is obtained. This forms a pale yellow, crystalline, insoluble powder melting at 212° ; it is unchanged by boiling alcoholic potassium hydroxide, is oxidised by chromic acid to sulphuric and hydrochloric acids and anthraquinone, and is reduced by zinc and acetic acid to a substance with acid properties which still contains sulphur and chlorine.

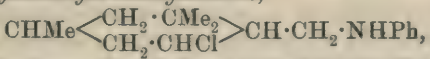
On allowing the interaction of sulphur monochloride and anthracene to proceed until the evolution of hydrogen chloride ceases, β-dichloroanthracene (m. p. 209°) and sulphur are formed. K. J. P. O.

Triphenylmethyl. By MOSES GOMBERG (*Ber.*, 1901, **34**, 2726—2733. Compare this vol., i, 77, 319, 638).—The hydrocarbon triphenylmethyl, CPh_3, can be isolated in small, colourless crystals by the action of acetone on a concentrated solution of triphenylchloromethane in benzene, or in long, colourless crystals by the action of ethyl formate ; it soon becomes yellow, reacts vigorously with iodine, absorbs oxygen readily, forming triphenylmethyl peroxide, and melts at 125—128° ; two molecular-weight determinations in freezing naphthalene gave M = 330 and 372 (calc. 243). The crystalline hydrocarbon dissolved in benzene gives about 86 per cent. of the theoretical yield of peroxide when exposed to air; the residue consists chiefly of an oil containing C, 84·20; H, 6·97; O, 8·83 per cent. T. M. L.

Action of Alcoholic Silver Nitrate on Aromatic Bases. By WILHELM VAUBEL (*Chem. Zeit.*, 1901, **25**, 739—740. Compare Lachowicz, Abstr., 1890, 445; Jörgensen, *ibid.*, 1886, 857; Hoogewerff and van Dorp, *ibid.*, 1881, 109; Mixter, *J. Amer. Chem. Soc.*, 1878, 1, 239).—When an alcoholic solution of silver nitrate is added to a similar solution of an aromatic base, a precipitate is produced consisting of a compound of 1 mol. of silver nitrate with 2 mols. of the base. Benzidine, tolidine, phenylacridine, β-naphthylamine, pyridine, and quinoline behave in this way. No compounds have been obtained with *p*-toluidine or indigotin. *o*-Toluidine gives a compound, the composition of which corresponds best with the formula $AgNO_3,3C_7H_7\cdot NH_2$. Aniline, acetanilide, and mono- and di-alkyl derivatives of aniline are more or less decomposed by alcoholic silver nitrate, the alkyl compounds yielding blue substances. J. J. S.

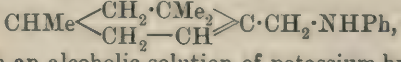
Tetrahydrobenzylamine Derivatives. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 119879).—The unsaturated *base*  $C_8H_{14}<\begin{array}{l}C\cdot CH_2\cdot NHPh\\ \| \\ CH\end{array}$ is obtained by converting the saturated hydroxyamine,  $C_8H_{14}<\begin{array}{l}CH\cdot CH_2\cdot NHPh\\ | \\ CH\cdot OH\end{array}$ (compare following abstract), into the *chloro*-base,  $C_8H_{14}<\begin{array}{l}CH\cdot CH_2\cdot NHPh\\ | \\ CHCl\end{array}$, by the action of phosphorus pentachloride and hydrogen chloride in benzene solution, and subsequently heating the halogen derivative at 130°; under these conditions, the substance undergoes rearrangement, and yields the hydrochloride of the new base. The free amine forms colourless crystals, melts at 38°, and boils at 211—213° under 20 mm. pressure.

Chlorotrimethylhexahydrobenzylaniline,



$$CHMe<\begin{array}{l}CH_2\cdot CMe_2\\ CH_2\cdot CHCl\end{array}>CH\cdot CH_2\cdot NHPh,$$

produced from hydroxytrimethylhexahydrobenzylaniline by the action of phosphorus pentachloride and hydrogen chloride, is a yellow oil yielding *trimethyltetrahydrobenzylaniline,*

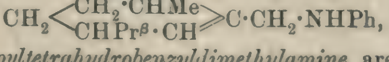


$$CHMe<\begin{array}{l}CH_2\cdot CMe_2\\ CH_2—CH\end{array}\gg C\cdot CH_2\cdot NHPh,$$

when heated with an alcoholic solution of potassium hydroxide; the unsaturated base is a colourless oil boiling at 187° under 19 mm. pressure.

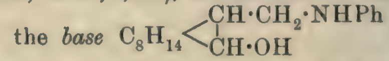
The *cis*- and *trans*-hydroxymethyl*iso*propylhexahydrobenzylamines yield chloro-bases which, by loss of hydrogen chloride, give rise to the same *methyl*iso*propylhexahydrobenzylamine*; this is an oily base resembling coniine, and boils at 230° under the ordinary pressure.

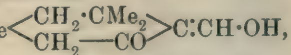
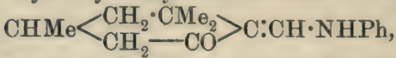
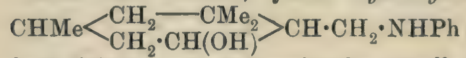
*Methyl*iso*propyltetrahydrobenzylaniline,*

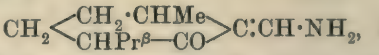
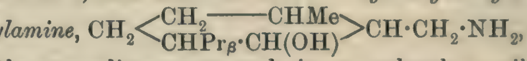


$$CH_2<\begin{array}{l}CH_2\cdot CHMe\\ CHPr^\beta\cdot CH\end{array}\gg C\cdot CH_2\cdot NHPh,$$

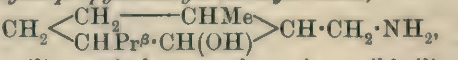
and *methyl*iso*propyltetrahydrobenzyldimethylamine* are oils boiling respectively at 193° under 11 mm., and at 124—128° under 13 mm. pressure. G. T. M.

Hydroxyhexahydrobenzylamine Derivatives. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 119862).—Anilinomethylenecamphor (compare Abstr., 1895, i, 63), when reduced with sodium and ethyl alcohol, yields the *base*  $C_8H_{14}<\begin{matrix}CH\cdot CH_2\cdot NHPh\\ |\\ CH\cdot OH\end{matrix}$; this is a colourless syrup, which boils at 231° under 30 mm. pressure and yields a crystalline, sparingly soluble hydrochloride.

Hydroxymethylenedihydroisophorone,  $CHMe<\begin{matrix}CH_2\cdot CMe_2\\ CH_2—CO\end{matrix}>C\colon CH\cdot OH$, separates in the form of its *sodium* derivative when dihydro*iso*phorone is heated with amyl formate and sodium ethoxide suspended in dry ether; the ketone set free by dilute acetic acid boils at 124° under 27 mm. pressure, and is a colourless oil having an odour resembling that of hydroxymethylenementhone. *Anilinomethylenedihydro*iso*phorone*,  $CHMe<\begin{matrix}CH_2\cdot CMe_2\\ CH_2—CO\end{matrix}>C\colon CH\cdot NHPh$, produced by boiling the preceding compound with a solution of aniline in methyl alcohol and acetic acid, is a yellow, crystalline substance, which, on reduction with sodium and alcohol, yields *hydroxytrimethylhexahydrobenzylaniline*,  $CHMe<\begin{matrix}CH_2——CMe_2\\ CH_2\cdot CH(OH)\end{matrix}>CH\cdot CH_2\cdot NHPh$; this product crystallises from light petroleum in colourless needles, melts at 68—70°, and boils at 221° under 15 mm. pressure.

Aminomethylenementhone,  $CH_2<\begin{matrix}CH_2\cdot CHMe\\ CHPr^{\beta}—CO\end{matrix}>C\colon CH\cdot NH_2$, crystallises from a solution of hydroxymethylenementhone in concentrated aqueous ammonia, and melts at 115°. *Hydroxymethyl*iso*propylhexahydrobenzylamine*,  $CH_2<\begin{matrix}CH_2——CHMe\\ CHPr_{\beta}\cdot CH(OH)\end{matrix}>CH\cdot CH_2\cdot NH_2$, obtained by reducing the preceding compound, is a colourless oil boiling at 150—152° under 30 mm. pressure; it solidifies on cooling. The crude reduction product is a mixture of two stereoisomeric bases, which are separated by saturating its benzene solution with hydrogen chloride. The hydrochloride of the *trans*-base separates, whilst that of the *cis*-base remains dissolved. The two modifications solidify, after rectification, to a mass of white crystals; the *trans*-base boils at 163°, and the *cis*-base at 165—170° under 30 mm. pressure.

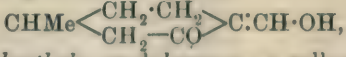
*Hydroxymethyl*iso*propylhexahydrobenzylaniline*,



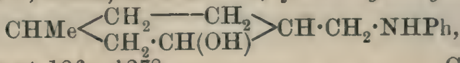
$$CH_2<\begin{matrix}CH_2——CHMe\\ CHPr^{\beta}\cdot CH(OH)\end{matrix}>CH\cdot CH_2\cdot NH_2,$$

prepared from anilinomethylenementhone, is an oil boiling at 247—248° under 20 mm. pressure. *Hydroxymethyl*iso*propylhexahydrobenzyldimethylamine* is obtained from *dimethylaminomethylenementhone* (an oily ketone forming a crystalline hydrate), and boils at 140° under 14 mm. pressure. *Hydroxymethyl*iso*propylhexahydrobenzylethylamine* boils at 165—166° under 19 mm. pressure.

*Hydroxymethylmethylene*cyclo*hexanone*,

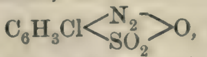


$$CHMe<\begin{matrix}CH_2\cdot CH_2\\ CH_2—CO\end{matrix}>C\colon CH\cdot OH,$$

yields *anilinomethylmethylene*cyclo*hexanone*, a yellow, crystalline ketone melting at 170—171°, which, on reduction, yields *hydroxymethylhexahydrobenzylaniline*,  $CHMe<\begin{smallmatrix}CH_2\text{——}CH_2\\CH_2\cdot CH(OH)\end{smallmatrix}>CH\cdot CH_2\cdot NHPh$, a crystalline base melting at 126—127°. G. T. M.

Action of Aminosulphonic Acid on *p*-Chloroaniline. By Carl Paal (*Ber.*, 1901, **34**, 2748—2757. Compare Abstr., 1894, i, 365; 1896, i, 235; 1897, i, 351).—The first product of the interaction of aminosulphonic acid and *p*-chloroaniline is *p*-chloroaniline aminosulphonate; when heated above its melting point (160°), this salt decomposes with the production of ammonium *p*-chlorophenylaminosulphonate and *p*-chloroaniline *p*-chlorophenylaminosulphonate, together with ammonium sulphate and *p*-chloroaniline sulphate. The *p*-chlorophenylaminosulphonates, when heated at 230—250°, are converted into *p*-chloroaniline-*o*-sulphonates by a transference of the SO_3H group from the nitrogen atom of the aniline to a carbon atom of the benzene ring in the ortho-position relatively to the amino-group.

p-*Chloroaniline aminosulphonate*, $C_6H_4Cl\cdot NH_2,NH_2\cdot SO_3H$, prepared by adding finely powdered aminosulphonic acid to an alcoholic solution of *p*-chloroaniline, crystallises from absolute alcohol in large, lustrous leaflets melting at 160°. *Ammonium* p-*chlorophenylaminosulphonate*, $C_6H_4Cl\cdot NH\cdot SO_3NH_4$, prepared by heating aminosulphonic acid with excess of *p*-chloroaniline, crystallises from alcohol in colourless, lustrous plates melting and decomposing at about 205°; the p-*chloroaniline* salt, $C_6H_4Cl\cdot NH\cdot SO_3H,C_6H_4Cl\cdot NH_2$, prepared by heating *p*-chloroaniline aminosulphonate at 160°, crystallises from alcohol in star-shaped aggregates of white needles decomposing at 190°; the *barium* salt, prepared by treating *p*-chloroaniline *p*-chlorophenylaminosulphonate with excess of concentrated aqueous barium hydroxide, crystallises in white needles and decomposes quantitatively into *p*-chloroaniline, sulphuric acid, and barium sulphate when boiled with hydrochloric acid; the *silver* salt is only obtainable from the free acid and silver carbonate and crystallises in white needles. p-*Chlorophenylaminosulphonic acid*, prepared from the barium salt, crystallises in concentric groups of white needles, which decompose at about 200°; on treatment with nitrous acid, it is converted into *p*-dichlorodiazoaminobenzene.

4-Chloroaniline-2-sulphonic acid is formed on heating *p*-chloroaniline aminosulphonate at 250°, but is best prepared by heating aminosulphonic acid at 230° with excess of *p*-chloroaniline. It crystallises in anhydrous needles or colourless plates, and decomposes at 280° (compare Claus and Mann, Abstr., 1891, 1488). The *barium* salt crystallises in prisms, and the *silver* salt in small needles. The *diazo*-compound,  $C_6H_3Cl<\begin{smallmatrix}N_2\\SO_2\end{smallmatrix}>O$, crystallises in pale yellow needles and is extremely stable; only by heating with alcohol under pressure at 110° is it converted into *m*-chlorobenzenesulphonic acid. The barium salt of this acid is found to crystallise with $1\frac{1}{2}H_2O$ (compare Kieselinsky, this Journ., 1876, i, 930).

Only once was a small quantity of 4-chloroaniline-3-sulphonic acid formed together with its isomeride on heating *p*-chloroaniline with aminosulphonic acid. The barium salt of this acid was found to crystallise with $5H_2O$ (compare Claus and Mann, *loc. cit.*); the *silver* salt forms short needles; the *diazo*-compound crystallises in white needles and is very stable. K. J. P. O.

Thiosulphonic Acids of Aromatic Amines and *m*-Diamines. CLAYTON ANILINE Co. (D.R.-P. 120504).—Aniline *o*-disulphide, $(S\cdot C_6H_4\cdot NH_2)_2$, the main product of the action of sulphur on aniline, when suspended in water and treated with excess of sulphur dioxide, yields aniline-*o*-thiosulphonic acid, a substance crystallising from water in colourless needles. This product, when boiled in acid or alkaline solutions, loses the elements of sulphur dioxide and regenerates the disulphide.

Aniline *p*-disulphide (Hofmann, Abstr., 1895, i, 87) yields aniline-*p*-thiosulphonic acid. Dimethylaniline disulphide also gives rise to the thiosulphonic acid on treatment with sulphur dioxide; this acid yields a nitroso-derivative and is readily decomposed by acids or alkalis, regenerating the disulphide.

m-Phenylenediamine and 2 : 4-tolylenediamine, when heated with sulphur at 60—120°, yield mixtures containing basic and non-basic constituents. The former, when treated with sulphur dioxide, give soluble derivatives, which are probably monothiosulphonic acids, whilst the latter yield dithiosulphonic acids. The *m*-phenylenediamine derivatives separate in colourless crystals, the corresponding tolylenediaminedithiosulphonic acid has not been obtained in a crystalline state. G. T. M.

Condensation Products of Aromatic Aldehydes with Primary Aromatic Amines and their Sulphonic Acids. JOHANN WALTER (D.R.-P. 118567).—Compounds of the benzylideneaniline type (azomethine derivatives $R'\cdot CH\colon NR''$) are obtained by oxidising a mixture of a tertiary base or a phenol and formaldehyde in the presence of an aromatic primary base or its sulphonic acid.

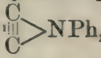
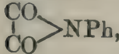
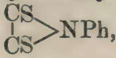
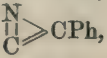
An aqueous solution of phenol, formaldehyde, and sodium *p*-toluidinesulphonate, when oxidised with cupric chloride, yields a precipitate consisting of sodium *p*-hydroxybenzylidene-p-toluidinesulphonate, $OH\cdot C_6H_4\cdot CH\colon N\cdot C_6H_3Me\cdot SO_3Na$, and its *o*-isomeride. These azomethine derivatives are hydrolysed by acids, yielding the corresponding aldehydes. The *compound* $OH\cdot C_{10}H_6\cdot CH\colon N\cdot C_7H_7$ results from the interaction of *β*-naphthol, formaldehyde, *p*-toluidine hydrochloride, and sodium chromate; it crystallises in pale yellow leaflets and when hydrolysed by mineral acids yields *p*-toluidine and *β*-hydroxynaphthaldehyde, $OH\cdot C_{10}H_6\cdot CHO$.

A mixture of dimethylaniline, formaldehyde, sodium *p*-toluidinesulphonate, and potassium dichromate gives rise to the *compound* $NMe_2\cdot C_6H_4\cdot CH\colon N\cdot C_7H_6\cdot SO_3H$, this substance on hydrolysis with acids yielding *p*-dimethylaminobenzaldehyde.

p-Nitrobenzyl alcohol, when oxidised in the presence of sulphanilic acid, furnishes the azomethine derivative,

$$NO_2\cdot C_6H_4\cdot CH\colon N\cdot C_6H_4\cdot SO_3H.$$

Similar condensation products of benzidine are obtained by treating this base either with homosaligenin, or with ethylaniline and formaldehyde in presence of an oxidising agent. When these products are hydrolysed, homosalicylaldehyde and *p*-ethylaminobenzaldehyde are respectively set free. G. T. M.

New Class of Organic Compounds. *iso*Nitriles and *cyclo*-Nitriles. By Alexander P. Sabanéeff and M. Prosin (*Bull. Soc. Chim.*, 1901, [iii], **25**, 823—828).—When a mixture of aniline with acetylene dibromide, acetylene tetrabromide, or bromoacetylene dibromide is treated with alcoholic potash, acetylenetriphenyltriamine, $C_2H_2(NHPh)_2{:}NPh$, and *phenyldicarbylamine*,  $\begin{array}{c}C\\ \vert\vert\vert\\ C\end{array}\!\!>NPh$, are produced. The latter substance was obtained as an oily liquid which readily oxidised on exposure to air with the formation of a crystalline *compound*,  $\begin{array}{c}CO\\ \vert\\ CO\end{array}\!\!>NPh$, convertible into oxanilic acid on treatment with water. On heating with sulphur, phenyldicarbylamine is converted into dithio-oxanilide and *dithio-oxanil*,  $\begin{array}{c}CS\\ \vert\\ CS\end{array}\!\!>NPh$, which, however, could not be obtained in the pure state. When heated with copper powder at 200—205°, dithio-oxanil yields a substance which is probably the nitrile,  $\begin{array}{c}N\\ \vert\vert\\ C\end{array}\!\!\geqslant CPh$, isomeric with phenyldicarbylamine. N. L.

Preparation of 4-Nitro-α-Naphthylamine and its Alkyl Derivatives from 1-Chloro-4-nitronaphthalene. Chemische Fabrik Griesheim-Elektron (D.R.-P., 117006. Compare Eng. Pat. 7692 of 1900).—1-Chloro-4-nitronaphthalene, when heated at 180—200° with an alcoholic solution of ammonia, ethylamine, or benzylamine, yields either 4-nitro-α-naphthylamine or the corresponding *ethyl* or *benzyl* derivative. The former of these secondary amines crystallises in dark red needles melting at 176—177° and having a blue fluorescence, whilst the latter melts at 156°. This reaction does not occur when the chlorine atom is situated in positions 5 or 8 with respect to the nitro-group. G. T. M.

Transformation of Hydroxynaphthalene Derivatives into the Corresponding Amines. Badische Anilin- & Soda-Fabrik (D.R.-P. 117471).—The formation of amines from phenols is greatly facilitated when the ammonia reacts in the presence of ammonium sulphite; a mixed sulphite, $OR{\cdot}SO_2{\cdot}NH_4$, is formed as an intermediate product, and this is subsequently converted by the excess of ammonia into the required amino-derivative, $R{\cdot}NH_2$. In the case of β-naphthol, the reaction takes place at 100—150°.

2 : 3-Dihydroxynaphthalene, when heated at 80° with ammonium sulphite solution and saturated with ammonia gives rise to a mixture of 2 : 3-aminohydroxynaphthalene and the corresponding diamine. 1 : 5-Dihydroxynaphthalene, when heated with these reagents at 125°, yields 1 : 5-diaminonaphthalene; this base is also obtained from 5-amino-α-naphthol.

Sodium α-naphthol-4-sulphonate at 100—150° yields α-naphthylamine-4-sulphonic acid. The sulphite of α-naphthol-7-sulphonic acid readily yields α-naphthylamine-7-sulphonic acid when heated at 100—110° with excess of ammonia (compare Eng. Pat. 1387 of 1900). 1 : 5-Dihydroxynaphthalene-7-sulphonic acid, when subjected to this process, furnishes the corresponding aminonaphtholsulphonic acid.

Resorcinol behaves like the dihydroxynaphthalenes and gives either *m*-aminophenol or *m*-phenylenediamine, according to the quantities of ammonia and sulphite employed. G. T. M.

8 : 8′-Dihydroxy-2 : 2′-dinaphthylamine-6 : 6′-disulphonic Acid. Farbenfabriken vorm. F. Bayer & Co. (D.R.-P. 121094. Compare D.R.-P. 114974).—8 : 8′-*Dihydroxy*-2 : 2′-*dinaphthylamine*-6 : 6′-*disulphonic acid*, $NH[C_{10}H_5(OH)\cdot SO_3H]_2$, prepared by heating sodium 8-hydroxy-β-naphthylamine-6-sulphonate with water at 200°, is a white, crystalline substance readily dissolving in water and forming soluble alkali salts which are precipitated by sodium chloride. The aqueous solution of the sodium salt exhibits a faint violet fluorescence.

G. T. M.

Phenanthrylamines. By Alfred Werner and J. Kunz (*Ber.*, 1901, **34**, 2524—2528).—When 3-hydroxyphenanthrene (3-phenanthrol) (Pschorr and Sumuleanu, Abstr., 1900, i, 488) is heated with sodium acetate, ammonium chloride, and glacial acetic acid for 9 hours at 280—300°, 3-*acetylaminophenanthrene* (*acetyl*-3-*phenanthrylamine*) is obtained in yield equal to 75 per cent. of the theoretical. It melts at 200—201°, and when hydrolysed yields 3-*aminophenanthrene* (3-*phenanthrylamine*), β, which melts at 87·5°. An isomeric 3-*aminophenanthrene*, α, melting at 143°, is obtained in 15 per cent. yield when the hydroxyphenanthrene is heated with aqueous ammonia and ammonium chloride at 200—220°. Each isomeride forms a hydrochloride and is regenerated unchanged from this; when treated with acetic anhydride, however, both yield the same acetyl derivative, described above.

When phenanthrene is sulphonated according to Graebe's directions, an insoluble barium sulphonate is formed amongst other products. From this, 2-hydroxyphenanthrene (2-phenanthrol) melting at 169° can be prepared. When the last substance is heated with sodium acetate, ammonium chloride, and acetic acid at 290°, 2-*acetylaminophenanthrene* (*acetyl*-2-*phenanthrylamine*) is obtained in 50 per cent. yield. It melts at 225—226° and is hydrolysed by hydrochloric acid in strong acetic acid solution at 100° to 2-*aminophenanthrene* (2-*phenanthrylamine*), which melts at 85°.

It was not found possible to diazotise either of the aminophenanthrenes. C. F. B.

Phenyl Carbonates. Chemische Fabrik von Heyden (D.R.-P. 117346. Compare Farbenfabriken vorm. F. Bayer & Co., this vol., i, 662).—The additive compounds of the pyridine bases with carbonyl chloride react with the phenols, yielding the corresponding phenyl carbonates. The pyridine carbonyl chloride compound, when treated in benzene or xylene solution with phenol or *o*-cresol, gives rise to phenyl carbonate or *o*-tolyl carbonate respectively; guaiacol carbonate may be similarly prepared. The analogous derivatives of 2-lutidine and 2-picoline behave in a similar manner. G. T. M.

Chlorocarbonates of Alcohols, Phenols, and their Derivatives. Farbenfabriken vorm. F. Bayer & Co. (D.R.-P. 118536. Compare this vol., i, 662, and D.R.-P. 114025).—The chlorocarbonates, RO·COCl, may be prepared by the action of carbonyl chloride on the corresponding hydroxy-compound, R·OH, in the presence of antipyrine or one of its analogues dissolved in benzene. Ethyl, benzyl, and phenyl chlorocarbonates are readily obtained in this manner. G. T. M.

Chlorocarbonates of Alcohols and Phenols and their Derivatives. Farbenfabriken vorm. F. Bayer & Co. (D.R.-P. 118537. Compare preceding abstract, and D.R.-P. 109933 and 114025).—*Salol chlorocarbonate*, $CO_2Ph·C_6H_4·O·COCl$, prepared by the interaction of salol and hexachlorodimethyl carbonate in a xylene solution of quinoline, separates from light petroleum in white crystals and melts at 90—91°. The hexachlorodimethyl carbonate may be replaced by carbonyl chloride or perchloromethyl formate, and other tertiary bases, such as antipyrine or dimethylaniline, may be substituted for quinoline; the bases of the pyridine series, however, are not suitable for this reaction. G. T. M.

Physical Isomerism of Thallium Picrate. By W. O. Rabe (*Zeit. physikal. Chem.*, 1901, **38**, 175—184).—When thallium picrate is crystallised from 96 per cent. alcohol, a mass of slender yellow needles is first thrown down. If these are left a few days in contact with the solution, small, red, shining crystals are formed between the yellow ones. Analysis and examination of their properties show that both the yellow and the red crystals are thallium picrate. The two modifications differ, not only in colour, but in specific gravity, in crystalline form, and in solubility. The sp. gr. of the yellow crystals (as determined by the suspension method) is 2·993 at 17°, that of the red crystals is 3·164 at 17°. The yellow crystals are thin, long needles, whilst the red crystals are either long prisms or plates; the crystallographic measurements are recorded in the paper. The difference of solubility (whether in water or methyl alcohol) is not large, but the solubility curves for both solvents cut each other at 46°, which is therefore the temperature of transition of the red into the yellow modification. When heated at 130°, the red crystals are transformed into the yellow crystals in a few seconds; the reverse change takes place very slowly below 40°, but is accelerated by light or the presence of a little solvent. J. C. P.

Action of Bromine on Carvacrol in the Presence of Aluminium Bromide. By F. Bodroux (*Bull. Soc. Chim.*, 1901, [iii], **25**, 818).—The action of bromine on carvacrol in the presence of aluminium bromide leads to the formation of nearly the theoretical quantity of *tetrabromo-*o*-cresol*, which crystallises in long, white, silky needles melting at 208°. N. L.

Primary Aminobenzohydrols. Kalle & Co. (D.R.-P. 119461). —Aminobenzohydrols are produced by heating either a mixture of an aromatic aldehyde and a primary base or the corresponding azomethine derivative in an alcoholic solution of a mineral acid. 4-*Nitro*-4′-*aminobenzohydrol*, $NO_2\cdot C_6H_4\cdot CH(OH)\cdot C_6H_4\cdot NH_2$, produced in this way either from *p*-nitrobenzylideneaniline or a mixture of its generators, forms a yellow, crystalline powder, melts at 240°, and is insoluble in the ordinary solvents, but dissolves readily in a mixture of glacial acetic and hydrochloric acids. G. T. M.

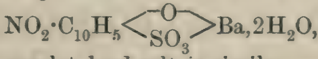
Preparation of 4-Nitro-α-naphthol and its Ethers from 1-Chloro-4-nitronaphthalene. Chemische Fabrik Griesheim-Elektron (D.R.-P. 117731).—1-Chloro-4-nitronaphthalene, when heated at 150—155° with sodium hydroxide dissolved in dilute alcohol, yields 4-nitro-α-naphthol; the methyl and ethyl ethers of this naphthol are obtained when the reaction is performed in methyl and ethyl alcohols respectively. G. T. M.

α-Naphthol Ethyl Ether and its Derivatives. By Otto N. Witt and Franz Schneider (*Ber.*, 1901, **34**, 3171—3191).—Details are given for preparing 1-ethoxynaphthalene from α-naphthol and potassium ethyl sulphate, this method being more advantageous than direct ethylation by means of alcohol and sulphuric acid (Gattermann, *Annalen*, 1888, **244**, 72); the ether, as obtained hitherto, has always been contaminated with α-naphthol, and the last traces of the latter are only removed by distilling in a vacuum and adding sufficient diazobenzenesulphonic acid and dilute alkali to form the tetrazo-dye derived from the naphthol. Thus purified, 1-ethoxynaphthalene melts at 5·5°, and boils at 276·4° (corr.) under 760 mm., at 276·6° (corr.) under 766 mm., at 185° (corr.) under 19 mm., and at 106—106·5° under 2 mm. pressure. The refractive indices for the principal lines of the spectrum are given; n_D is 1·59916, and the dispersion quotient is 21·0; the sp. gr. at 19° is 1·061.

Heermann's method of preparing 1-ethoxynaphthalene-4-sulphonic acid (Abstr., 1894, i, 251) is modified on account of the need of removing unchanged naphthol ether from the product; the sulphonic acid and its salts dissolve this in considerable quantity, and it is best removed by extracting the acid thoroughly with chloroform. The pure acid is crystallised from water at 50°, and forms large, four-sided plates with $2H_2O$, which become anhydrous in a desiccator; the *ammonium* salt is anhydrous, the *potassium* crystallises with $1H_2O$, the *sodium* salt with $5H_2O$ or anhydrous, the *barium* salt with $1H_2O$, and the *strontium* salt with $2H_2O$. 1-*Ethoxynaphthalene*-4-*sulphonic chloride* crystallises from ether or light petroleum in six-sided, yellowish plates, and melts at 101°; the *sulphonamide* crystallises from alcohol in stout, white needles, and melts at 167°; the *sulphanilide*, from the same solvent, forms flat needles and melts at 178°. The *ethyl* ester forms long prisms melting at 102—103°, and the *methyl* ester colourless leaflets melting at 105—106°.

By cold acetic anhydride, the sulphonic acid is converted into the mixed *anhydride*, $OEt\cdot C_{10}H_6\cdot SO_2\cdot OAc$, which forms thick, transparent crystals, is decomposed by water and alcohol, and in the air is transformed, initially, apparently into the anhydride, $O_2(SO_2\cdot C_{10}H_6\cdot OEt)_2$, with loss of acetic anhydride, and ultimately into 1-ethoxynaphthalene-4-sulphonic acid.

Phenylnaphthionic acid, $NHPh\cdot C_{10}H_6\cdot SO_3H$, is better obtained by first gently warming and then boiling a solution of 1-ethoxy-4-naphthalenesulphonic acid in an excess of aniline for a quarter of an hour, than by the German Patent 70349; if, however, the solution is boiled too long, sulphanilic acid and α-naphthylphenylamine are formed, whilst if the solution of the acid in aniline is boiled at once after being made, sulphanilic acid and α-naphthol ethyl ether are formed without any phenylnaphthionic acid. Similar results were obtained with *p*-toluidine; p-*tolylnaphthionic acid* crystallises from water in long, rectangular, anhydrous plates and melts at 194°

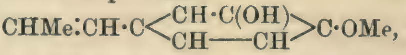
Instead of yielding 4-nitro-1-ethoxynaphthalene alone, the action of nitric acid (1 mol.) on 1-ethoxynaphthalene-4-sulphonic acid (compare Heermann, *loc. cit.*) gives a molecular compound of it with dinitro-α-naphthol; by adding carbamide, however, to the nitric acid, even if the latter be in excess, the formation of dinitro-α-naphthol is prevented, and 4-nitro-1-ethoxynaphthalene is obtained along with 2-*nitro*-1-*ethoxynaphthalene*-4-*sulphonic acid*. The *potassium* salt of the latter crystallises in large, thick plates and prisms, and when heated with concentrated hydrochloric acid at 150—160° for 2 hours, yields 2-nitro-α-naphthol, thus proving the constitution of the acid. Using boiling concentrated aqueous potassium hydroxide for the hydrolysis, *dipotassium* 2-*nitro-α-naphthol*-4-*sulphonate* is obtained in orange-yellow, silky needles or thick prisms; the *monopotassium* salt forms long, lemon-yellow needles. The *barium* salt,  $NO_2\cdot C_{10}H_5{<}\begin{smallmatrix}O\\SO_3\end{smallmatrix}{>}Ba,2H_2O$, is very sparingly soluble in water, and the scarlet *lead* salt is similar. W. A. D.

8-Hydroxy-α-naphthylamine-4-sulphonic Acid. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 120016).—The *sulphurous* ester, $SO_3H\cdot C_{10}H_5(NH_2)\cdot O\cdot SO_2H$, is produced on heating 1 : 8-diaminonaphthalene-4-sulphonic acid with either the bisulphite compound of acetone or a mixture of sodium, hydrogen sulphite, acetone, and sodium hydroxide, the reaction being carried out in concentrated aqueous solutions; the ester is very soluble in water, and, unlike the hydroxynaphthylaminesulphonic acid, yields a normal diazonium derivative which combines with phenols forming azo-colouring matters.

8-Hydroxy-α-naphthylamine-4-sulphonic acid is obtained on hydrolysing the preceding compound with alkali hydroxides. G. T. M.

2 : 3-Dicyanoquinol. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 117005).—2 : 3-Dicyanoquinol, prepared by adding a concentrated potassium cyanide solution to a solution of quinone in alcoholic sulphuric acid and precipitating with excess of acid, crystallises from water in yellow needles. Two mols. of the quinone take part in the reaction, the second being reduced to quinol. When warmed with concentrated sulphuric acid, the dicyanoquinol yields *p*-dihydroxyphthalimide. G. T. M.

***Iso*Chavibetol.** CÆSAR POMERANZ (D.R.-P. 119253).—*Propenylcatechol ethoxymethyl ether*, $CHMe\colon CH\cdot C_6H_4(OMe)\cdot O\cdot CH_2\cdot OEt$, the methyl ether of ethoxy*iso*eugenol, results from the methylation of the latter phenol by the action of methyl iodide and aqueous sodium hydroxide solution; it is a colourless, refractive liquid boiling at 160—162° under 14 mm. pressure.

iso*Chavibetol*,  $\mathrm{CHMe{:}CH{\cdot}C}{<}\begin{matrix}\mathrm{CH{\cdot}C(OH)}\\ \mathrm{CH{-\!-\!-}CH}\end{matrix}{>}\mathrm{C{\cdot}OMe}$, produced by heating the preceding compound with a dilute solution of hydrochloric acid in alcohol and water, melts at 92° and boils at 147° under 14 mm. pressure; it has a pleasant odour resembling that of vanilla and clove. G. T. M.

Tetrahydrodiphenylene Oxide. By Otto Hönigschmid (*Monatsh.*, 1901, **22**, 561—576).—*Tetrahydrodiphenylene oxide*, $C_{12}H_{12}O$, is prepared by reducing diphenylene oxide by excess of sodium and absolute alcohol, and is a heavy, colourless oil, boiling at 268—269°, which dissolves in sulphuric acid with a red colour; from this solution, water throws down a bluish-violet oil. The *picrate*, $C_{18}H_{15}O_8N_3$, crystallises in orange-yellow needles melting at 91°. When a smaller quantity of sodium is used in the reduction, a mixture of crystals melting at 43° and oil is obtained; in this mixture probably unchanged diphenylene oxide and dihydrodiphenylene oxide are present, together with the tetrahydro-derivative.

Tetrahydrodiphenylene oxide is oxidised by potassium permanganate to diphenylene oxide; by fused potassium hydroxide, it is converted into 1-hydroxydiphenyl (m. p. 56°; compare Graebe, Abstr., 1895, i, 372).

1-*Hydroxydiphenyl acetate*, $C_{12}H_9{\cdot}OAc$, crystallises in colourless needles. 1-*Ethoxydiphenyl*, $C_{12}H_9{\cdot}OEt$, crystallises in lustrous prisms melting at 34° and boiling at 276°; the *methoxy*-derivative forms lustrous prisms melting at 29° and boiling at 274°.

By treating an additive product of tetrahydrodiphenylene oxide and bromine with alcoholic potash, hydrogen bromide is eliminated, and a small quantity of an oil is obtained which boils at 278° and is probably dihydrodiphenylene oxide.

In attempting to prepare phenylene-α-naphthylene oxide by Arx's method (Abstr., 1881, 282), the author obtained only α-dinaphthylene oxide (m. p. 178—179°) which has properties identical with those hitherto ascribed to phenylene-α-naphthylene oxide. On reduction with sodium and amyl alcohol, *octahydrodinaphthylene oxide*, $C_{20}H_{20}O$, is formed, crystallising in colourless needles which melt at 128° and exhibit a feeble blue fluorescence. K. J. P. O.

Alkylation of Hydroxyquinol [1 : 2 : 4-Hydroxybenzene]. By E. Brezina (*Monatsh.*, 1901, **22**, 590—600. Compare this vol., i, 534).—The action of ethyl bromide or iodide and potassium hydroxide on 1 : 2 : 4-triacetoxybenzene yields a yellow oil insoluble in potassium hydroxide. When this oil was distilled under a pressure of 20 mm., distillation began at 150° and was stopped at 200°, on the appearance of signs of decomposition.

From the residue there separated crystals of *hexaethoxydiphenyl*, $C_{12}H_4(OEt)_6$, representing 2·5 to 2·7 per cent. of the triacetoxybenzene used. This compound crystallises in triclinic plates or white needles melting at 100—102°, and dissolving in sulphuric acid with a red colour which becomes green on heating. On treatment with hydriodic acid, a *hexahydroxydiphenyl* is obtained which decomposes at about 200°, and does not appear to be identical with δ-hexahydroxydiphenyl (Barth and Schreder, Abstr., 1885, 520). On acetylation, two substances are formed, a hexa-acetoxydiphenyl (m. p. 169—172°), probably identical with the acetyl derivative of δ-hexahydroxydiphenyl, and *tetra-acetoxydiphenylene oxide*, $C_{12}H_4O(OAc)_4$, which melts at 240—245°.

From the distillate, triethoxybenzene separated on cooling; the remaining oil was fractionated under 15 mm. pressure. The first fraction boiling at 130—135°, was mainly 1 : 4-diethoxybenzene (m. p. 68—70°). From the fraction boiling at 155—165° was isolated *triethoxyethylbenzene*, $C_6H_2Et(OEt)_3$, which forms crystals melting at 31—32° and boils at 157—160° under 18 mm. pressure. *Dibromotriethoxyethylbenzene*, $C_6Br_2Et(OEt)_3$, prepared from the last-mentioned compound, forms crystals melting at 65—67°. K. J. P. O.

Derivatives of Hydroxyquinol. By JOHANNES THIELE and KARL JAEGER (*Ber.*, 1901, **34**, 2837—2842).—The *tribenzoyl* derivative of hydroxyquinol crystallises in lustrous leaflets, melts at 120°, and is hydrolysed much less readily than the triacetyl derivative. Hydroxyquinol, when treated with nitric acid, yields oxalic acid, but the triacetyl derivative gives nitranilic acid. When the triacetyl derivative is nitrated in the presence of acetic anhydride, a *nitro*-derivative, $C_{12}H_{11}O_8N$, is obtained, which crystallises from dilute alcohol in long, white needles and melts at 107—108°; when hydrolysed, it yields *nitrohydroxyquinol*, $C_6H_5O_5N$, which forms yellowish-red crystals decomposing between 200° and 220°, and when treated with bromine is converted into tribromohydroxyquinone.

Dibromonitrohydroxyquinol, $C_6H_3O_5NBr_2$, obtained by treating nitrohydroxyquinol dissolved in carbon disulphide with bromine, crystallises from benzene in microscopic needles and melts and decomposes at 164°. *Tribromohydroxyquinol*, $C_6H_3O_3Br_3$, obtained by reduction of tribromohydroxyquinone, crystallises from benzene in small, reddish needles which turn brown at 110° and decompose at 120°, and forms a *triacetyl* derivative which crystallises in white needles and melts at 189°.

Hydroxyquinolcarboxylic acid, $C_7H_6O_5$, obtained by the action of sodium hydrogen carbonate and carbon dioxide on the hydroxyquinol, crystallises from water in needles with $\frac{1}{2}H_2O$, melts and decomposes at 217—218°, gives a greenish coloration with concentrated sulphuric acid, and forms a *triacetyl* derivative which crystallises in plates or needles and melts at 162—163°. When reduced with sodium amalgam, both hydroxyquinol and hydroxyquinolcarboxylic acid yield the dihydroresorcinol described by Merling (Abstr., 1894, i, 177).

R. H. P.

p-**Hydroxytriphenylcarbinol.** By AUGUSTIN BISTRZYCKI and CARL HERBST (*Ber.*, 1901, **34**, 3073—3079. Compare this vol., i, 716).—p-*Hydroxytriphenylcarbinol*, $OH\cdot C_6H_4\cdot CPh_2\cdot OH$, is produced when *p*-hydroxytriphenylacetic acid is slowly added to cold concentrated sulphuric acid, the action being accompanied by an evolution of carbon monoxide; it crystallises from dilute acetic acid, or from benzene and petroleum, in pale yellow or colourless plates, and decomposes at 70°. At this temperature, 2 mols. of the substance lose the elements of water, and yield p-*hydroxytriphenylmethyl ether*, $O(CPh_2{\cdot}C_6H_4{\cdot}OH)_2$, a substance crystallising from ether in needles and melting at 70°. The ether closely resembles the carbinol in physical properties, and is readily transformed into the latter compound on treatment with dilute acetic acid; both substances are soluble in warm potassium hydroxide solutions. p-*Acetoxytriphenylcarbinol*, $OAc{\cdot}C_6H_4{\cdot}CPh_2{\cdot}OH$, obtained by warming the carbinol with acetic anhydride and dry sodium acetate, crystallises in small plates and melts at 136°; it is insoluble in cold dilute potassium hydroxide solution.

p-*Acetoxytriphenylmethyl ether*, $O(CPh_2{\cdot}C_6H_4{\cdot}OAc)_2$, produced either by acetylating *p*-hydroxytriphenylmethyl ether or by treating the corresponding carbinol with acetic anhydride containing a trace of sulphuric acid, crystallises in hexagonal plates and melts at 136—137°. It closely resembles the preceding compound.

p-*Benzoxytriphenylcarbinol*, $OBz{\cdot}C_6H_4{\cdot}CPh_2{\cdot}OH$, prepared by the Schotten-Baumann reaction, forms prisms melting at 132°; like the corresponding acetoxy-compound, it is insoluble in solutions of the alkali hydroxides. The m-*nitro*-derivative crystallises in aggregates of needles and melts at 150°.

Dibromo-p-*hydroxytriphenylcarbinol*, $OH{\cdot}C_6H_2Br_2{\cdot}CPh_2{\cdot}OH$ and carbon monoxide are the products of the action of concentrated sulphuric acid on dibromo-*p*-hydroxytriphenylacetic acid at 50°. The carbinol crystallises from glacial acetic acid in four-sided plates and melts at 225°; it is very sparingly soluble in dilute potassium hydroxide solution.

Dibromo-p-*acetoxytriphenylmethyl ether*, $O(CPh_2{\cdot}C_6H_2Br_2{\cdot}OAc)_2$, prepared by warming the preceding compound with acetic anhydride and sodium acetate, crystallises in plates and melts at 171°. G. T. M.

Carbinol Compounds of Triphenylmethane and its Derivatives. By JOSEF HERZIG and P. WENGRAF (*Monatsh.*, 1901, **22**, 601—614. Compare Abstr., 1894, i, 336; 1896, i, 486).—It has been shown that in the two triacetylaurins the presence of a hydroxyl group cannot be demonstrated, and it has been suggested that one of the benzene neuclei is in the quinone form and that, consequently, no hydroxyl group is present (*loc. cit.*). Similar observations have been made by Döbner in the case of benzaurin (Abstr., 1883, 861). The ethyl derivatives of tetramethyldiaminotriphenylcarbinol and of hexamethyltriaminotriphenylcarbinol are, however, true ethoxy-compounds.

Although with alcohol and dilute acids (best a 3 per cent. alcoholic solution of hydrogen chloride) triphenylcarbinol yields an ethoxy-derivative with great ease, with alkalis and alkyl iodide, no alkyl derivative can be prepared. The alkyl ethers are readily hydrolysed by acids, but not by alkalis. The acetyl derivative (Allen and Kölliker, Abstr., 1885, 655), by mere recrystallisation from alcohol, is quantitatively transformed into the ethyl ether, whilst the latter, by the action of acetic anhydride or acetyl chloride, can be converted into the acetyl derivative. The carbinol itself can only be acetylated by means of acetyl chloride. In these properties, triphenylcarbinol does not resemble any known hydroxyl compounds.

In the acetylation of rosolic acid by sodium acetate and acetic anhydride, besides the *triacetate*, $C_{20}H_{15}O_5Ac_3$ (crystals melting at 167—168°), there was obtained a very small quantity of a substance melting at 144—146°. From benzaurin, on acetylation, a *diacetate*, $C_{19}H_{14}O_3Ac_2$, is readily obtained, which melts at 144—146°, and on reduction with zinc and acetic acid yields diacetoxytriphenylmethane (m. p. 108—110°). Döbner (*loc. cit.*) describes a diacetate of benzaurin which melts at 116—119°; the authors were only able to obtain this compound once in ten attempts. K. J. P. O.

Mixed Acid Anhydrides. Knoll & Co. (D.R.-P. 117267).—The mixed anhydrides of the organic acids are readily prepared by mixing an acid or its salt with an acid chloride dissolved in an indifferent solvent containing a tertiary base. Benzoyl acetate is obtained from acetyl chloride and benzoic acid or benzoyl chloride and acetic acid in the presence of pyridine, and boils at 125—140° under 17 mm. pressure. Under similar conditions, *ethyl benzoyl carbonate*, $Bz{\cdot}CO_2Et$, and *dibenzoyl carbonate*, $COBz_2$, are produced by the interaction of benzoic acid with ethyl chlorocarbonate and carbonyl chloride respectively; these compounds are oils, the latter readily decomposing into carbon dioxide and benzoic anhydride.

The action of ethyl chlorocarbonate on salicylic acid gives rise to two compounds, *ethyl salicyl monocarbonate*, $CO_2H{\cdot}C_6H_4O{\cdot}CO_2Et$, and *diethyl salicyl dicarbonate*, $CO_2Et{\cdot}O{\cdot}C_6H_4{\cdot}CO_2{\cdot}CO_2Et$; the latter is a neutral oil. *Ethyl cinnamyl carbonate*, $CHPh{:}CH{\cdot}CO_2{\cdot}CO_2Et$, and *ethyl valeryl carbonate* and valeryl acetate are produced in a similar manner. Quinoline or dimethylaniline may be employed instead of pyridine. G. T. M.

Disulphones. VII. Mercaptoles and Disulphones of the Ketonic Acids and the Sulphur Acids obtained from them. By Theodor Posner (*Ber.*, 1901, **34**, 2643—2673. Compare Abstr., 1900, i, 5).—The nature and stability of the mercaptoles and disulphones formed from the ketonic esters and the mercaptans are influenced both by the nature of the mercaptan and by that of the ketonic ester. Derivatives of the substituted esters are both less easily produced and less stable. Characteristic differences also show themselves in the behaviour on hydrolysis.

[With Alex. Deinhardt.]—Lævulic acid readily undergoes condensation with benzyl mercaptan in acetic acid solution in presence of hydrogen chloride, with formation of *γ-dithiobenzylvaleric acid* (lævulic benzylmercaptole), $CMe(SC_7H_7)_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, melting at 70°. Oxidation converts it into *γ-dibenzylsulphonevaleric acid* (lævulic benzyldisulphone), $CMe(SO_2{\cdot}C_7H_7)_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, which crystallises in silky needles and plates and melts and decomposes at 143—145°. With amyl mercaptan, lævulic acid yields *γ-dithioamylvaleric acid*, $CMe(SC_5H_{11})_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, which can only be obtained as an oil. The corresponding *γ-diamylsulphonevaleric acid*, $CMe(SO_2\cdot C_5H_{11})_2\cdot CH_2\cdot CH_2\cdot CO_2H$, crystallises in slender needles melting at 98—100°; the *barium* salt is sparingly soluble. *γ-Dithiophenylvaleric acid*, $CMe(SPh)_2\cdot CH_2\cdot CH_2\cdot CO_2H$, crystallises in rectangular tablets, probably belonging to the monoclinic system, which melt at 67°. On oxidation with permanganate in acetic acid solution, it yields *γ-diphenylsulphonevaleric acid*, $CMe(SO_2Ph)_2\cdot CH_2\cdot CH_2\cdot CO_2H$, as a crystalline powder melting at 140°.

Ethyl lævulate also reacts with the mercaptans, yielding the ethyl esters of the acids just described, and these are converted by oxidation into the corresponding sulphones. All these esters are converted by hydrolysis into the corresponding acids. *Ethyl γ-dithiobenzylvalerate*, $CMe(SC_7H_7)_2\cdot CH_2\cdot CH_2\cdot CO_2Et$, is an oil, whilst *ethyl γ-dibenzylsulphonevalerate* forms slender crystals melting at 118—119°. *Ethyl γ-dithioamylvalerate* is a colourless oil, whilst *ethyl γ-diamylsulphonevalerate* crystallises in triclinic prisms melting at 46°. *Ethyl γ-dithiophenylvalerate* is also an oil, whilst *ethyl γ-diphenylsulphonevalerate* forms small crystals melting at 112—113°.

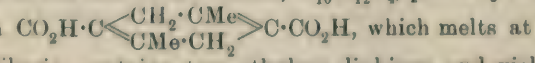
The derivatives of ethyl acetoacetate differ from those of ethyl lævulate in their behaviour on hydrolysis, unsaturated compounds being formed. *Ethyl β-dithiobenzylbutyrate*, $CMe(SC_7H_7)_2\cdot CH_2\cdot CO_2Et$, is an oil, and yields on hydrolysis *β-thiobenzyl*isocrotonic *acid*, $C_7H_7\cdot S\cdot CMe\colon CH\cdot CO_2H$, which melts at 125° and decomposes at 146—150°. *Ethyl β-dibenzylsulphonebutyrate*,

$$CMe(SO_2C_7H_7)_2\cdot CH_2\cdot CO_2Et,$$

forms a loose, easily electrified powder, which sinters at 138—139°, and melts at 141—142°. On hydrolysis, it yields some benzyl mercaptan, together with an oily acid which slowly decomposes, yielding a neutral substance which melts at 104—105°. The nature of these products has not yet been ascertained. *Ethyl β-dithioamylbutyrate* is also an oil, and is converted by hydrolysis into *thioamyl*isocrotonic *acid*, $C_5H_{11}\cdot S\cdot CMe\colon CH\cdot CO_2H$, which crystallises in prisms melting at 96°. *Ethyl β-diamylsulphonebutyrate* is a colourless oil; the only product of hydrolysis which could be isolated was amylsulphinic acid. The derivatives of phenyl mercaptan have previously been described by Baumann and Escales (Abstr., 1886, 879) and Autenrieth (Abstr., 1891, 204).

[With O. Claudius.]—The mercaptoles derived from alkylacetoacetic esters are only oxidised to sulphones with great difficulty. *Ethyl β-dithiobenzyl-α-methylbutyrate*, $CMe(S\cdot C_7H_7)_2\cdot CHMe\cdot CO_2Et$, melts at 78°. On hydrolysis, it yields the corresponding *acid*, which melts at 131—133°. *Ethyl β-dibenzylsulphone-α-methylbutyrate*,

$$CMe(SO_2\cdot C_7H_7)_2\cdot CHMe\cdot CO_2Et,$$

melts at 130°; the only product of hydrolysis which could be isolated was benzoic acid. *Ethyl β-dithioamyl-α-methylbutyrate* is an oil, and yields no well characterised products on hydrolysis. *Ethyl β-diamylsulphone-α-methylbutyrate* is also an oil, and on hydrolysis yields an acid of the molecular formula, $C_{10}H_{12}O_4$, probably having the constitution  $CO_2H\cdot C{<}\begin{matrix}CH_2\cdot CMe\\ CMe\cdot CH_2\end{matrix}{>}C\cdot CO_2H$, which melts at 234°. This acid is dibasic, contains two ethylene linkings, and yields a *tetrabromide* melting at 204°, whilst the *methyl ester* is crystalline and melts at 148°. *Ethyl β-dithiophenyl-α-methylbutyrate* melts at 49° and on hydrolysis yields *β-thiophenyl-α-methyl*iso*crotonic acid*,

$$\mathrm{SPh{\cdot}CMe{:}CMe{\cdot}CO_2H}.$$

Ethyl β-diphenylsulphone-α-methylbutyrate melts at 130° and on hydrolysis yields an acid which could not be procured pure.

Ethyl β-dithiobenzyl-α-ethylbutyrate is an oil which on hydrolysis yields the saturated *β-dithiobenzyl-α-ethylbutyric* acid melting at 86—87°. The corresponding *sulphone*, $\mathrm{CMe(SO_2{\cdot}C_7H_7)_2{\cdot}CHEt{\cdot}CO_2Et}$, melts at 97°, and yields benzoic acid on hydrolysis. *Ethyl β-dithioamyl α-ethylbutyrate* is an oil and yields no definite compound on hydrolysis. The corresponding *sulphone* is also an oil, which is probably converted by hydrolysis into a mixture of amylsulphinic acid and *β-amylsulphone-α-ethyl*iso*crotonic acid*. The mercaptole and disulphone of ethyl ethylacetoacetate and phenyl mercaptan have previously been described by Autenrieth. The mercaptole ester is converted by hydrolysis into *β-thiophenyl-α-ethyl*iso*crotonic acid*, $\mathrm{SPh{\cdot}CMe{:}CEt{\cdot}CO_2H}$, which melts very indefinitely at 88—100°. The products of hydrolysis of the sulphone have not been isolated.

[With A. Ebers.]—*Ethyl β-dithioethyl-α-dimethylbutyrate*,

$$\mathrm{CMe(SEt)_2{\cdot}CMe_2{\cdot}CO_2Et},$$

is a colourless oil; the corresponding *disulphone* crystallises in short, thick prisms melting at 131—133°, and is converted by hydrolysis into the free *acid*, which crystallises in microscopic needles and melts at 102—103°. *Ethyl β-dithiobenzyl-α-dimethylbutyrate* is a heavy oil, whilst the corresponding *disulphone* melts at 130—136°, and yields benzoic acid on hydrolysis. *Ethyl β-dithioamyl-α-dimethylbutyrate* and the corresponding *disulphone* are both oils. The condensation product of ethyl dimethylacetoacetate and phenyl mercaptan is converted by oxidation into phenyl disulphide, no disulphone being formed.

Ethyl β-dithioethyl-α-diethylbutyrate, $\mathrm{CMe(SEt)_2{\cdot}CEt_2{\cdot}CO_2Et}$, is an unstable oil and is converted by oxidation into the *sulphone* which has not been obtained pure. The *benzylmercaptole* is also an oil, and is converted by oxidation into benzyl sulphone. The *amylmercaptole* is also an oil, and yields an oily *disulphone* which has not been obtained pure. The *phenylmercaptole* is an oil from which no disulphone could be obtained by oxidation, the only products isolated being phenyl disulphide and ethyl diethylacetoacetate. A. H.

Acetyl- and Benzoyl-iminodithiocarbonic Esters. By Henry Lord Wheeler and Treat B. Johnson (*Amer. Chem. J.*, 1901, **26**, 185—206).—*Methyl acetyliminodithiocarbonate*, $\mathrm{NAc{:}C(SMe)_2}$, prepared from sodium methyl acetyliminodithiocarbonate and methyl iodide in alcoholic solution, is an oil boiling at 142—144° under 20 mm. pressure. iso*Amyl acetyldithiocarbamate*, $\mathrm{NHAc{\cdot}CS{\cdot}SC_5H_{11}}$, prepared from *iso*amyl thiocyanate and thioacetic acid, crystallises from alcohol in yellow plates and melts at 84°; when dissolved in alcoholic sodium ethoxide and treated with *iso*amyl bromide, it gave iso*amyl acetyliminodithiocarbonate*, $\mathrm{C_{13}H_{25}ONS_2}$, as an oil boiling at 198—200° under 20 mm. pressure. Methyl benzoyliminodithiocarbonate, $\mathrm{NBz{:}C(SMe)_2}$, and the ethyl ester, are decomposed by hydrochloric acid to the mercaptan and methyl or ethyl benzoylthiolcarbamate, $NHBz\cdot CO\cdot SMe$, or $NHBz\cdot CO\cdot SEt$. *Methyl ethyl benzoyliminothiocarbonate,*

$$NBz\colon C(SMe)\cdot SEt,$$

prepared from ethyl benzoyliminodithiocarbonate and methyl iodide or from the methyl ester and ethyl iodide, is an oil which boils at 224° under 20 mm. pressure and is apparently hydrolysed by hydrochloric acid to a mixture of methyl and ethyl benzoylthiolcarbamates; when warmed with aniline, it gave methyl and ethyl mercaptides, and a solid which crystallised from alcohol in flattened prisms, melted constantly at 79—80°, and appeared to be a mixture of the two compounds previously obtained in a similar manner from the dimethyl and diethyl compounds (Wheeler and Merriam, Abstr., 1901, i, 515). *Propyl benzoyliminothiocarbonate,* $NBz\colon C(SPr^{a})_2$, is a pale yellow oil which boils at 238—239° under 20 mm. pressure. iso*Amyl benzoyldithiocarbamate,* $NHBz\cdot CS\cdot SC_5H_{11}$, crystallises from dilute alcohol in yellow prisms and melts at 48—49°. *Benzyl ethyl benzoyliminodithiocarbonate,* is an oil which does not crystallise and cannot be distilled without decomposition. The *dibenzyl* ester, $NBz\colon C(S\cdot CH_2Ph)_2$, crystallises from alcohol in long, silky needles, melts sharply at 97°, and has an odour suggestive of roses or carnations. p-*Nitrobenzyl benzoyliminodithiocarbamate,* $NHBz\cdot CS\cdot S\cdot CH_2\cdot C_6H_4\cdot NO_2$, crystallises from alcohol in clusters of short, yellow needles, and melts at 155—156°. p-*Bromobenzyl benzoyldithiocarbamate,* $NHBz\cdot CS\cdot S\cdot CH_2\cdot C_6H_4Br$, separates from alcohol as a yellow, crystalline powder and melts at 126°. *Benzyl-*p-*nitrobenzyl benzoyliminodithiocarbonate,*

$$NBz\colon C(S\cdot CH_2Ph)\cdot S\cdot CH_2\cdot C_6H_4\cdot NO_2,$$

crystallises from alcohol in short needles, and melts at 84—85°.

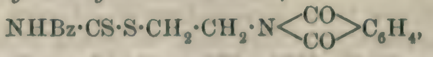
Carbethoxymethyl benzyl benzoyliminodithiocarbonate,

$$NBz\colon C(S\cdot CH_2Ph)\cdot S\cdot CH_2\cdot CO_2Et,$$

prepared from ethyl chloroacetate and benzyl benzoyldithiocarbamate, crystallises from alcohol in colourless, flattened prisms and melts at 79°. An *isomeric* compound, $NHBz\cdot CS\cdot S\cdot CH(CH_2Ph)\cdot CO_2Et$, was, however, obtained on benzylating the carbethoxymethyl ester; this also melts at 79°, but a mixture of the isomerides melts at 63°; it crystallises from alcohol in bunches of bright yellow prisms.

Phenyl thiocyanoacetate, $NCS\cdot CH_2\cdot CO_2Ph$, prepared from phenyl chloroacetate and potassium thiocyanate, crystallises from dilute alcohol in colourless plates, sinters at 28°, and melts at 31—32°. *Carbophenoxymethyl benzoyldithiocarbamate,* $NHBz\cdot CS\cdot S\cdot CH_2\cdot CO_2Ph$, crystallises from alcohol and melts at 127—129°. *α-Carbethoxyethyl benzyl benzoyliminodithiocarbonate,* $NBz\colon C(S\cdot CH_2Ph)\cdot S\cdot CHMe\cdot CO_2Et$, prepared from the monobenzyl ester and ethyl α-bromopropionate, forms colourless prisms and melts at 105—106°; the product from the interaction of benzyl chloride and the α derivative of ethyl propionate and benzoyldithiocarbamate melts at 105—106°, and appears to be isomeric with the preceding compound.

Phthaliminoethyl benzoyldithiocarbamate,



$$NHBz\cdot CS\cdot S\cdot CH_2\cdot CH_2\cdot N{<}{\genfrac{}{}{0pt}{}{CO}{CO}}{>}C_6H_4,$$

forms yellow needles and melts at 178—182°. By the action of benzyl chloride, it is converted into *phthaliminoethyl benzyl benzoyliminodithio-*

carbonate, $NBz\colon C(S\cdot CH_2Ph)\cdot S\cdot CH_2\cdot CH_2\cdot N\colon(CO)_2\colon C_6H_4$, which crystallises from alcohol in colourless needles and melts at 119—120° ; it could not be prepared from the benzyl compound and bromoethylphthalimide.

a-Thiocyanoethylbenzene, $CHMePh\cdot SCN$, is a colourless oil and boils at 157—159° under 36 mm. pressure.

Desyl thiocyanate, $CHPhBz\cdot SCN$, from bromodeoxybenzoin and potassium thiocyanate, crystallises from alcohol in colourless prisms and melts at 110—111°.

ω-m-*Xylyl thiocyanate*, $C_6H_4Me\cdot CH_2\cdot SCN$, is an oil which boils at 147° under 12 mm. pressure. m-*Xylyl benzoyldithiocarbamate*, $NHBz\cdot CS\cdot S\cdot CH_2\cdot C_6H_4Me$, crystallises from alcohol in bright-yellow, needle-like prisms and melts at 93—94°. *Benzyl* m-*xylyl benzoyliminodithiocarbonate*, $NBz\colon C(S\cdot CH_2Ph)\cdot S\cdot CH_2\cdot C_6H_4Me$, prepared from benzyl benzoyldithiocarbamate and *m*-xylyl bromide, crystallises from alcohol and melts constantly at 97—98° ; *m*-xylyl benzoyldithiocarbamate and benzyl chloride gave a compound melting at 85—89·5°, which seems to be an isomeride of the preceding compound, but did not melt like a pure substance.

m-*Xylyl mercaptan*, $C_6H_4Me\cdot CH_2\cdot SH$, is a colourless oil which boils at 215—217° under atmospheric pressure. *Benzyl* m-*xylyl sulphide*, $C_6H_4Me\cdot CH_2\cdot S\cdot CH_2Ph$, is a colourless oil boiling at 193—196° under 15 mm. pressure.

Dixylyl benzoyliminodithiocarbonate crystallises from alcohol in colourless prisms and melts at 89·5—90°.

Mesityl thiocyanate, $C_6H_3Me_2\cdot CH_2\cdot SCN$, crystallises from dilute alcohol in colourless plates and melts at 58°.

Mesityl benzoyldithiocarbamate, $NHBz\cdot CS\cdot S\cdot CH_2\cdot C_6H_3Me_2$, crystallises from alcohol in yellow plates or leaflets and melts at 114·5°.

Benzyl mesityl benzoyliminodithiocarbonate, prepared from the preceding compound and benzyl chloride, or from benzyl benzoyldithiocarbamate and mesityl bromide, crystallises from alcohol in prisms, and melts at 117·5°. T. M. L.

Nitrohydroxylaminic Acid. By FRANCESCO ANGELICO and S. FANARA (*Gazzetta*, 1901, **31**, ii, 15—40).—The sodium salt of this acid can be obtained in a purer state than by Angeli's method (Abstr., 1897, ii, 24) by replacing the ethyl nitrate by a methyl alcoholic solution of methyl nitrate. The potassium salt, $K_2N_4O_3$, forms a white, crystalline powder readily soluble in water. On treating solutions of the salts of nitrohydroxylaminic acid with silver nitrate, a voluminous yellow precipitate is obtained, rapidly changing to grey owing to separation of metallic silver, nitric oxide being at the same time evolved. The ammonium and hydrazine salts could not be prepared. The *calcium* ($3\frac{1}{2}H_2O$), *strontium* ($1\frac{1}{2}H_2O$), *barium* ($1H_2O$), *cadmium* ($1H_2O$), *lead*, and *cerium* $[Ce_2(N_2O_3)_2,Ce(OH)_5]$ salts are described; they all decompose on heating, giving in some cases the metallic oxide and nitric oxide. With the sodium salt, however, the initial phase of the decomposition results in the formation of a mixture of nitrite and hyponitrite of sodium. If the decomposition of the salts is carried out in presence of aldehydes the $\colon NOH$ group combines with the aldehydes forming hydroxamic acids, the reaction taking place readily and in most cases giving theoretical yields.

Benzhydroxamic acid, $C_7H_7O_2N$, obtained by heating benzaldehyde with sodium nitrohydroxylaminate and precipitating the acid in the form of its barium salt, crystallises from ether in white needles which melt and decompose at 129—131°. With copper acetate, it gives a pale green salt, and with ferric chloride an intense cherry-red coloration. When boiled with dilute sulphuric acid, it is resolved into benzoic acid and hydroxylamine; this reaction serves as a means of detection of small quantities of aldehydes.

Anishydroxamic acid, $C_8H_9O_3N$, prepared in a similar way, crystallises from acetone in sparkling scales melting and decomposing at 165°. With copper acetate, ferric chloride, and boiling dilute sulphuric acid, it behaves similarly to benzhydroxamic acid.

Piperonylhydroxamic acid, $C_8H_7O_4N$, separates from acetone in white crystals melting and decomposing at 172—173°, and gives the characteristic reactions of the hydroxamic acids.

The ethyl ether of salicylaldehyde gives the corresponding *hydroxamic acid*, $C_9H_{11}O_3N$, which separates from a mixture of benzene and ether in white needles melting at 139°. With ferric chloride and copper acetate, it gives the characteristic reactions.

Neither *o*-nitrobenzaldehyde nor nitropiperonaldehyde reacts with salts of nitrohydroxylaminic acid.

m-*Nitrobenzhydroxamic acid*, $C_7H_6O_4N_2$, separates from benzene in small, white crystals melting and decomposing at 153°.

Bromopiperonylhydroxamic acid, $C_8H_6O_4NBr$, is deposited from acetone in minute crystals melting and decomposing at 180°. It is slowly attacked when boiled with dilute sulphuric acid, yielding hydroxylamine and *bromopiperonylic acid* melting at 202°.

m-*Nitrosobenzhydroxamic acid* crystallises from ether in needles which melt and decompose at 73—76° and are soluble in alkalis; at the ordinary temperature, it quickly decomposes, yielding a black resin and hence could not be analysed.

Hepthydroxamic acid, $C_7H_{15}O_2N$, crystallises from benzene in shining, white scales melting at 75—76°. When boiled with dilute sulphuric acid, this acid yields hydroxylamine and heptoic acid.

Formhydroxamic and acethydroxamic acids may be prepared by this method, and also the hydroxamic acids corresponding with propaldehyde, butaldehyde, and valeraldehyde.

Glyoxal yields a hydroxamic acid. *Suberyldihydroxamic acid* melts and decomposes at 135° and when boiled with dilute sulphuric acid yields suberic acid and hydroxylamine. T. H. P.

Phenoxyacetic Anhydride. Chemische Fabrik auf Aktien (Schering) (D.R.-P. 120772).—*Phenoxyacetic anhydride*,

$$O(CO\cdot CH_2\cdot OPh)_2,$$

prepared by heating sodium phenoxyacetate with phosphorus oxychloride dissolved in toluene, crystallises from ether in white, lustrous needles and melts at 67—69°; it dissolves in the ordinary organic solvents and is only slowly hydrolysed when boiled with water, in which it is insoluble. G. T. M.

o-Toluoyl Chloride: Esters of Anthranilic Acid. By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1901, **25**, 793).—I. o-Toluoyl chloride boils at 209° and the corresponding cyanide at 221°; on hydrolysis, it yields o-toluoylformic acid, which when distilled is converted into o-toluic acid. o-*Toluoylformamide* melts at 130°. ω-*Chloro*-o-*toluoyl chloride*,

$$CH_2Cl\cdot C_6H_4\cdot COCl,$$

distils at 265°, but cannot be transformed into the corresponding cyanide.

II. Esters of anthranilic acid are best prepared by reducing the esters of nitrobenzoic acids with tin and hydrochloric acid. Only the methyl ester has a pleasant odour. The ester from fermentation amyl alcohol boils at 294° and has a feeble odour. *Methyl* o-*nitrophenylacetate* is a yellow liquid boiling at 264°. J. J. S.

Methyl Anthranilate. ERNST ERDMANN & HUGO ERDMANN (D.R.-P. 120120. Compare D.R.-P. 110386).—Methyl o-nitrobenzoate, produced by methylating o-nitrobenzoic acid with methyl alcohol and sulphuric acid, boils at 150·5° under 10 mm. pressure, has a sp. gr. 1·289 at 16°, and yields methyl anthranilate when reduced with stannous chloride, zinc dust or iron, and hydrochloric acid.

G. T. M.

Alkyl Carboxyanthranilates from Phthalimide Derivatives containing Halogen Radicles attached to Nitrogen. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 119661).—Alkyl carboxyanthranilates, $CO_2R\cdot C_6H_4\cdot NH\cdot CO_2R$, are readily prepared without the formation of bye-products by the action of dilute alcoholic solutions of sodium methoxide and ethoxide on phthalbromoimide or its chlorine analogue. The *dimethyl* ester, $CO_2Me\cdot C_6H_4\cdot NH\cdot CO_2Me$, resulting from the employment of sodium methoxide in methyl alcohol, crystallises in needles, melts at 60—61°, and boils at 165—166° under 12 mm. pressure; it is readily soluble in the ordinary organic solvents. The corresponding *diethyl* ester melts at 43—44° and boils at 174° under 10 mm. pressure. G. T. M.

Alkyl Acetylphenylglycine-o-carboxylates. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 117059).—*Diethyl acetylphenylglycine*-o-*carboxylate* results from the action of acetyl chloride or anhydride on diethyl phenylglycine-o-carboxylate [or of alcoholic hydrogen chloride below 50° on acetylphenylglycine-o-carboxylic acid (Eng. Pat. 6628 of 1900)]; it forms lustrous crystals and melts at 62°. The *dimethyl* ester melts at 82—83°. G. T. M.

ω-Cyanomethylanthranilic Acid (Nitrile of Phenylglycine-o-carboxylic Acid). FARBWERK MÜHLHEIM VORM. A. LEONHARDT & Co. (D.R.-P. 117924).—ω-*Cyanomethylanthranilic acid*,

$$CO_2H\cdot C_6H_4\cdot NH\cdot CH_2\cdot CN,$$

readily obtained by treating an alcoholic or aqueous solution of anthranilic acid hydrochloride in succession with potassium cyanide and formaldehyde, crystallises from water and melts at 184°; this compound is also formed on mixing the reagents in 50 per cent. acetic acid or in benzene. G. T. M.

Phenylglycine-*o*-carboxylic Acid from Anthranilic Acid. Farbwerk Mühlheim vorm. A. Leonhardt & Co. (D.R.-P. 120105).—*ω-Cyanomethylanthranilic acid*, $CO_2H\cdot C_6H_4\cdot NH\cdot CH_2\cdot CN$, prepared by adding formalin solution (1 mol. of formaldehyde) to an aqueous solution containing equivalent amounts of anthranilic acid hydrochloride, and potassium cyanide, separates as a white, voluminous precipitate soluble in alkalis and reprecipitated by acids; it crystallises from alcohol and melts at 184°.

The *amide* of phenylglycine-*o*-carboxylic acid is obtained on dissolving the nitrile in concentrated sulphuric acid, allowing the mixture to remain for 24 hours, and pouring the product on to ice; it crystallises from water and melts at 195° (compare Vorländer and Weissbrenner, Abstr., 1900, i, 295). The *thioamide* of the same acid results from the action of ammonia and yellow ammonium sulphide solution on the nitrile; it crystallises from water and melts at 190°. G. T. M.

Neutral Esters of Phenylglycine-*o*-carboxylic Acid. Farbwerk Mühlheim vorm. A. Leonhardt & Co. (D.R.-P. 120138. Compare preceding abstract).—ω-Cyanomethylanthranilic acid, when heated with an alcohol and a mineral acid, readily yields the corresponding neutral ester, $CO_2R\cdot C_6H_4\cdot NH\cdot CO_2R$, of phenylglycine-*o*-carboxylic acid. The *methyl* ester melts at 93—94° and the *ethyl* ester at 75°. G. T. M.

Synthesis and Products of Dehydration of Unsaturated Acids. By Marussia Bakunin (*Gazzetta*, 1901, **31**, ii, 73—84).—In preparing unsaturated acids by the dehydration of aldehydes or of acids of the type $CH_2R\cdot CO_2H$ by means of acetic anhydride or acid, the author finds that the resinous secondary products always obtained are decreased in quantity if the reaction is carried out in a current of dry carbon dioxide. Thus the yield of benzylidenemalonic acid obtained from malonic acid, benzaldehyde, and acetic acid is greatly increased if the materials be heated in an atmosphere of carbon dioxide.

The formation of allo-isomerides (compare Abstr., 1897, ii, 622 and 623; this vol., i, 84) seems to take place first at high temperatures. Thus, by heating benzylidenemalonic acid at 195°, small quantities of *allo*cinnamic acid are formed, whilst when the latter acid is heated with phosphoric oxide in chloroform solution it is apparently transformed, first into truxone, and on longer heating into indone. In the case of the ordinary cinnamic acid, heating with phosphoric oxide converts it into the anhydride, no truxone, but small quantities of a red substance melting at 170—180°, being obtained.

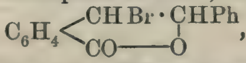
When benzaldehyde and sodium phenylacetate are heated together in a stream of carbon dioxide, phenylcinnamic acid is obtained in almost theoretical yield, together with small quantities of stilbene and of the allo-isomeride of the acid melting at 137°; *aniline* allo*phenylcinnamate*, $C_{15}H_{12}O_2,C_6H_7N$, separates from benzene in long, silky needles melting at 128°. *allo*Phenylcinnamic acid, when boiled in chloroform solution with phosphoric oxide, appears to yield first the anhydride, then, on further heating, a red compound, phenylindone, which is gradually transformed into phenyltruxone.

The yield of phenyl-*o*-nitrocinnamic acid is increased if it is formed in a current of carbon dioxide, but the formation of resinous products is not entirely prevented. In the preparation of phenyl-*m*-nitrocinnamic acid, the allo-isomeride is also formed; the former acid, when heated with phosphoric oxide in chloroform solution, yields, firstly, the *anhydride*, $C_{30}H_{20}O_7N_2$, which is deposited from acetone in white needles, and, later, the corresponding substituted *indone* crystallising from benzene in bright red plates melting at 218°. Phenyl-*p*-nitrocinnamic acid is obtained in almost theoretical yield when sodium phenylacetate and phenyl-*p*-nitrobenzaldehyde are heated at 210° in carbon dioxide. If the temperature is 160°, a certain amount of the allo-isomeric acid is formed, which is, however, decomposed at 200°. T. H. P.

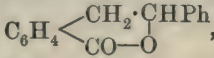
[Derivatives of] some Unsaturated Aromatic Acids. By ERNST LEUPOLD (*Ber.*, 1901, **34**, 2829—2837).—*Ammonium stilbene-o-carboxylate*, with H_2O, crystallises in lustrous prisms and the *silver* salt in a silvery, fan-shaped mass of crystals. When the acid is treated with nitrous acid, it yields a *dinitro*-derivative,

$$NO_2\cdot CHPh\cdot CH(NO_2)\cdot C_6H_4\cdot CO_2H,$$

which is a greenish, crystalline substance melting and decomposing at 123°, and, when boiled with acetic acid, forms nitrobenzalphthalide. The *dibromide* of stilbene-*o*-carboxylic acid is a white, crystalline substance which melts and decomposes at 180°; when boiled with acetic acid, it yields the *lactone*,



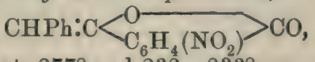
$C_6H_4{<}\begin{array}{l}CHBr\cdot CHPh\\ CO\text{——}O\end{array}$, which crystallises in silvery needles melting at 137°. When warmed with concentrated sulphuric acid, the acid yields the *lactone*,



$C_6H_4{<}\begin{array}{l}CH_2\cdot CHPh\\ CO\text{—}O\end{array}$, which crystallises in slender needles and melts at 89°.

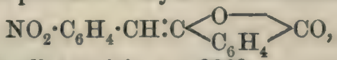
The *dibromide* of *o*-carboxycinnamic acid crystallises in small, colourless columns, melts at 189°, and when warmed with acetic acid yields phthalylacetic acid. *o*-Carboxycinnamic acid, when warmed with concentrated sulphuric acid, yields a lactonic acid, $C_{10}H_8O_4$ (either dihydro*iso*coumarincarboxylic acid or the lactone of α-benzylhydrylacetic acid), which forms a *barium* salt crystallising with $4H_2O$, a *silver* salt crystallising in silky needles, and an *ethyl* ester crystallising in slender needles.

A mixture of two *benzylidenenitrophthalides*,



$$CHPh{:}C{<}\begin{array}{c}O\\ C_6H_4(NO_2)\end{array}{>}CO,$$

melting respectively at 277° and 232—233°, was obtained by the condensation of 4-nitrophthalic anhydride and phenylacetic acid. *p*-Nitrophenylacetic acid and phthalic anhydride condense, forming m-*nitrobenzylidenephthalide*,



$NO_2\cdot C_6H_4\cdot CH{:}C{<}\begin{array}{c}O\\ C_6H_4\end{array}{>}CO$, which crystallises in brownish-yellow needles melting at 222°. R. H. P.

Formation of Substantive Azo-dyes from Di-*p*-aminophenylcyanobutadiene. By MARTIN FREUND (*Ber.*, 1901, **34**, 3109).—*p*-Nitrocinnamaldehyde and *p*-nitrobenzyl cyanide condense, forming *α-cyano-αδ-di-*p*-nitrophenyl-αγ-butadiene*,

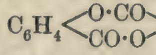
$$NO_2\cdot C_6H_4\cdot CH{:}CH\cdot CH{:}C(CN)\cdot C_6H_4\cdot NO_2,$$

which crystallises in small, yellow needles and melts at 276°; the corresponding *amino*-compound forms brownish-yellow crystals, melts at 196°, and yields substantive azo-dyes. R. H. P.

Synthesis of Tertiary Aromatic Acids. By AUGUSTIN BISTRZYCKI and K. WEHRBEIN (*Ber.*, 1901, **34**, 3079—3081. Compare this vol., i, 701, 716).—*Diphenyl*-p-*tolylacetic acid*, $C_6H_4Me\cdot CPh_2\cdot CO_2H$, and its homologues are readily prepared by condensing benzilic acid with toluene and other aromatic hydrocarbons in the presence of tin tetrachloride. This compound crystallises from dilute alcohol in spherical aggregates of colourless plates melting at 205°; its *silver* salt, $C_{21}H_{17}O_2Ag$, is a white, insoluble substance. G. T. M.

Benzyl Salicylate. AKTIEN-GESELLSCHAFT FÜR ANILINFABRIKATION (D.R.-P. 119463).—*Benzyl salicylate*, $OH\cdot C_6H_4\cdot CO_2\cdot CH_2Ph$, prepared by heating anhydrous potassium salicylate with benzyl chloride at 130—140° for 14 hours, is a colourless, odourless liquid boiling at 208° under 26 mm. pressure; it is scarcely soluble in water, but dissolves more readily in ether or alcohol. It yields sparingly soluble salts with the alkali hydroxides, and is hydrolysed into its generators by alcoholic potassium hydroxide solution. G. T. M.

New Crystallised Bismuth Salicylate. By PAUL THIBAULT (*Bull. Soc. Chim.*, 1901, [iii], **25**, 794—796).—The action of salicylic acid on hydrated bismuth oxide does not result in the formation of any pure compound, but if the yellow, crystalline anhydrous oxide, obtained by boiling bismuth nitrate solution with excess of alkali hydroxide, is employed, *bismuth salicylate*, $Bi_2O_3(C_7H_6O_3)_3$, is readily produced. It crystallises in small, anisotropic prisms melting and decomposing at 100°, is not acted on by cold alcohol or ether, and is slowly decomposed by cold, more quickly by hot, water. N. L.

Disalicylide. By ALFRED EINHORN and HERMANN PFEIFFER (*Ber.*, 1901, **34**, 2951—2953. Compare Anschütz, Abstr., 1893, i, 165).—*Disalicylide*,  $C_6H_4<\begin{matrix}O\cdot CO\\CO\cdot O\end{matrix}>C_6H_4$, is formed when carbonyl chloride is passed into an ice-cold solution of salicylic acid in pyridine, the operation lasting from 1 to 1·5 hours; the mixture is kept for several days, and then poured into ice-cold, extremely dilute sulphuric acid. It crystallises from acetic acid or chloroform in prismatic needles melting at 200—201°. It may be distilled without decomposition, is not decomposed by sodium hydroxide or carbonate solutions, and when heated with phenol for several hours at 200° yields salol.

Other *o*-hydroxy-acids may be converted into dianhydrides by similar methods.

o-*Dicresotide* melts at 213·5°, the meta-compound at 207·5°, and the para-isomeride at 243·5°. The bimolecular *anhydride* of mandelic acid melts at 240°, of benzilic acid at 196°, and of α-hydroxy*iso*butyric acid at 27·78°. J. J. S.

Condensation Products of the Haloid Derivatives of Hydroxytolualdehyde and Hydroxytoluic Acid with the Phenols. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 117890).—*p*-ω-Chloromethylsalicylic acid and β-naphthol, when boiled with glacial acetic acid, yield a crystalline *compound*, $CO_2H\cdot C_6H_3(OH)\cdot CH_2\cdot O\cdot C_{10}H_7$, melting at 198°; the corresponding *products* from phenol, *o*-cresol, and thymol melt at 159°, 226°, and 250° respectively. The *iso*butyl-*o*-cresol, resorcinol, pyrogallol, and guaiacol *compounds* melt at 177°, 249°, 243°, and 210° respectively. *p*-ω-Chloromethylsalicylaldehyde reacts in a similar manner (compare D.R.-P. 114194). G. T. M.

Acetyltropic Acid. By Oswald Hesse (*J. pr. Chem.* 1901, [ii], **64**, 286—288).—Under the influence of acetic anhydride or acetyl chloride, tropic acid in combination with alkaloids (of *Solanaceæ*) is readily converted into atropic acid. When warmed with acetic anhydride, tropic acid yields *acetyltropic acid*, $OAc\cdot CH_2\cdot CHPh\cdot CO_2H$, which forms flattened crystals melting at 80°. On boiling a solution of the acetyl derivative in potassium hydroxide, hydrolysis takes place, but atropic and not tropic acid is produced. K. J. P. O.

Preparation of Condensation Products from Substituted Hydroxybenzyl Haloids and Amines. Farbenfabriken vorm. F. Bayer & Co (D.R.-P. 121051. Compare D.R.-P. 113723 and 114194, and this vol., i, 727).—The *compound*,

$$CO_2H\cdot C_6H_3(OH)\cdot CH_2\cdot NH\cdot C_6H_4\cdot OEt,$$

prepared by condensing *p*-ω-chloromethylsalicylic acid,

$$CH_2Cl\cdot C_6H_3(OH)\cdot CO_2H,$$

and phenetidine in ethereal solution, crystallises in yellow needles and melts at 161°. This hydroxy-acid and dimethylamine give rise to the *compound* $NMe_2\cdot CH_2\cdot C_6H_3(OH)\cdot CO_2H$, a substance crystallising in colourless needles and melting at 210°.

p-ω-Chloromethylsalicylaldehyde and piperidine yield the *compound* $CHO\cdot C_6H_3(OH)\cdot CH_2\cdot C_5NH_{10}$, which forms a brownish-white, amorphous powder.

Methyl *o*-ω-chloromethyl-*p*-hydroxybenzoate, $CH_2Cl\cdot C_6H_3(OH)\cdot CO_2Me$, and dimethylamine yield the *methyl ester*, $NMe_2\cdot CH_2\cdot C_6H_3(OH)\cdot CO_2Me$, melting at 83°; the corresponding *ethyl* ester melts at 62°. G. T. M.

Preparation of *p*-Aminophenylglyoxylic Acid and its Homologues, and Substitution Products. C. F. Boehringer & Sons (D.R.-P. 117021. Compare Abstr., 1874, 421, and D.R.-P. 112174).—p-*Aminophenylglyoxylic acid* and its homologues and substitution products are readily obtained by oxidising *p*-aminophenyltartronic acid, $NH_2\cdot C_6H_4\cdot C(CO_2H)_2\cdot OH$, and its derivatives with manganese dioxide (Weldon mud), mercuric oxide, ferric cloride, potassium permanganate, or arsenious acid, in acid or in alkaline solution. *p*-Aminophenylglyoxylic acid, $NH_2\cdot C_6H_4\cdot CO\cdot CO_2H$, obtained from the potassium hydrogen salt of the corresponding tartronic acid, crystallises in yellow needles or lamellæ, and sinters at 190°; its *phenylhydrazone* crystallises in yellow needles and melts at 163—164°.

p-*Methylaminophenylglyoxylic acid* crystallises from water in orange-yellow prisms and melts at 155—157°; the phenylhydrazone melts at 166°. The corresponding *ethyl* derivative melts at 116°. *Diethylaminophenylglyoxylic acid*, $NEt_2\cdot C_6H_4\cdot CO\cdot CO_2H$, crystallises in yellow prisms and melts at 114—116°; the corresponding dimethyl compound (Abstr., *loc. cit.*) furnishes a phenylhydrazone sintering at

175° and melting at 181°. *Ethylene*-p-*diaminodiphenylglyoxylic acid*, $C_2H_4:N_2H_2(C_6H_4\cdot CO\cdot CO_2H)_2$, melts and decomposes at 205—208°. p-*Aminomethoxyphenylglyoxylic acid*, $NH_2\cdot C_6H_3(OMe)\cdot CO\cdot CO_2H$, melts at 147—148°. The *compound*, $NHPh\cdot C_6H_4\cdot CO\cdot CO_2H$, is tarry, but yields a *phenylhydrazone* melting at 168°. *Benzylmethylaminophenylglyoxylic acid*, $C_7H_7\cdot NMe\cdot C_6H_4\cdot CO\cdot CO_2H$, melts at 85—87°.

p-*Amino*-m-*tolylglyoxylic acid*, $NH_2\cdot C_7H_6\cdot CO\cdot CO_2H$, prepared from *p*-amino-*m*-tolyltartronic acid, crystallises in needles melting at 163—164°; the *phenylhydrazone* melts at 179°.

p-*Ethylamino*-m-*tolylglyoxylic acid*, $NHEt\cdot C_7H_6\cdot CO\cdot CO_2H$, forms yellow needles and melts at 132—134°. G. T. M.

_p_-Aminophenylglyoxylic Acid and its Derivatives. C. F. BOEHRINGER & SONS (D.R-P. 117168).—The condensation product of alloxan with an aromatic base (compare Pellizzari, Abstr., 1888, 142; also D.R.-P. 112174) is readily converted into the corresponding aminophenylglyoxylic acid by successive oxidation and hydrolysis, without isolation of the intermediate tartronic acid (compare preceding abstract).

p-Methylanilalloxan yields *p*-methylaminophenylglyoxylic acid when treated with mercuric oxide and sodium hydroxide. The acid $C_{11}H_{12}O_3N_2$, obtained from dimethylanilalloxan by the action of a 10 per cent. alkali solution, furnishes *p*-dimethylaminophenylglyoxylic acid when treated with manganese dioxide and sodium hydroxide. *p*-Amino-*m*-tolylglyoxylic acid, *p*-methylbenzylaminophenylglyoxylic acid, and *p*-dimethylaminobenzoylformic acid are also obtained by similar means from the corresponding alloxan derivatives. G. T. M.

Preparation of Indigo and its Derivatives from the Esters of Phenylglycine-_o_-carboxylic Acid. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 120321).—The mixed salts,

$$CO_2Et\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO_2Na,$$

and $CO_2Na\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO_2Et$, when treated in succession with acetic anhydride, sodium hydroxide, and atmospheric oxygen, yield indigo. The salt, $CO_2Me\cdot C_6H_3Cl\cdot NH\cdot CH_2\cdot CO_2H$, derived from *o*-nitro-*m*-chlorobenzoic acid under these conditions gives rise to dichloroindigo. G. T. M.

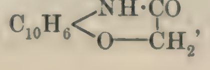
Preparation of Indigotin and its N-Alkyl Derivatives. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 120900).—An intimate mixture of sodium *o*-chlorobenzoate, glycine, and potassium or sodium hydroxide heated for some time at 150—250°, and subsequently dissolved in water saturated with carbon dioxide, yields indigotin on oxidation. When the glycine is replaced by its methyl or ethyl derivative, the corresponding N-alkylindigotins are produced. G. T. M.

Molecular Weight of Indigo-blue and of Indigo-red. By WILHELM VAUBEL (*Chem. Zeit.*, 1901, **25**, 725—726. Compare Sommaruga, Abstr., 1879, 63, 532).—The molecular weights of indigotin and indigo-red have been determined by the cryoscopic method in various solvents. Indigotin in *p*-toluidine or phenol gives results that point to the double molecular formula $C_{32}H_{20}O_4N_4$, but in aniline solution to the simple formula $C_{16}H_{10}O_2N_2$. Indigo-red in *p*-toluidine solution also appears to have the higher molecular weight, namely, 524. J. J. S.

Condensation of Indigo-white with Formaldehyde. Badische Anilin- & Soda-Fabrik (D.R.-P. 120318).—Indigo-white, when treated with formaldehyde in neutral aqueous or alcoholic solutions, yields an insoluble compound which separates as a green powder. The product is sparingly soluble in water, cold alcohol, ether, or the aromatic hydrocarbons, but dissolves more readily in acetone, glacial acetic acid, or hot alcohol; from the last of these, it separates in greenish-yellow leaflets melting at 215°, and gradually changes into indigo. It is readily decomposed into its generators by alkali carbonates or hydroxides at the ordinary temperature, and a similar hydrolysis occurs when it is boiled with water. G. T. M.

New Hydro-compound of Indigotin and its Application to Quantitative Estimation. By Wilhelm Vaubel (*Zeit. angew. Chem.*, 1901, **14**, 892—893).—When indigo is shaken with an alcoholic solution of potassium hydroxide of appropriate concentration and zinc dust, the dye rapidly dissolves, forming a deep-red solution. Excess of zinc dust finally bleaches this solution, with the production of indigo-white, whilst the access of air regenerates indigotin. Other reducing agents, as iron, ferrous sulphate, aluminium, &c., also bring about this phenomenon. The author expresses the opinion that there is formed an intermediate product, "dihydroindigotin," between indigotin and indigo-white, and suggests that its production may be used as a basis for a colorimetric estimation of commercial indigos.
K. J. P. O.

β-Naphthoxyacetic Acid and its Derivatives. By Fritz Spitzer (*Ber.*, 1901, **34**, 3191—3205).—Details are given for the preparation of β-naphthoxyacetic acid from β-naphthol and chloroacetic acid. The pure substance melts at 156°, not at 151—152° as given by Spica (Abstr., 1887, 495), and is not sensitive to light. It is best nitrated in glacial acetic acid solution, and not by the method of the German Patent 58614; the product is 1-*nitro-2-naphthoxyacetic acid*, which crystallises from the solvent in yellow needles, melts at 192°, and is not hydrolysed by acids or alkalis under pressure. An attempt to synthesise the nitro-compound from 1-nitro-β-naphthol and chloroacetic acid gave only a resinous product, but its structure follows from that of the derived aminónaphthoxyacetic acid (*infra*); the *ammonium* salt forms lustrous, yellow, rhombic plates, the *potassium* salt crystallises with $\frac{1}{2}H_2O$, and the *sodium* salt with $1H_2O$ in lustrous, yellow needles; the *ethyl* ester crystallises in lustrous, slightly yellow needles and melts at 100°, and the *chloride* in yellow plates melting at 94°; the *amide* and *anilide* separate from alcohol in needles and melt respectively at 189° and 139°.

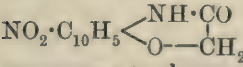
1-*Amino-2-naphthoxyacetic anhydride*,  $C_{10}H_6<\begin{matrix}NH\cdot CO\\ O—CH_2\end{matrix}$, obtained by

the reduction of the nitro-compound with stannous chloride and hydrochloric acid, crystallises from alcohol in white, lustrous needles and melts at 217°; it is not soluble in alkali carbonates, but yields crystalline *salts* with alkali hydroxides. It is not esterified by alcohol and hydrogen chloride, and cannot be hydrolysed.

1-*Acetylamino-2-naphthoxyacetic acid*, obtained by condensing 1-acetylamino-α-naphthol with chloroacetic acid by means of potassium hydroxide, separates from water in leaflets, melts at 234—235°, and yields an *ethyl* ester crystallising from alcohol in white needles and melting at 128°; the hydrolysis of the acetyl derivative by alkalis yields the foregoing 1-amino-2-naphthoxyacetic acid, thus proving the structure of the latter.

Trinitro-2-naphthoxyacetic acid, obtained by the nitration of the mononitro-compound dissolved in concentrated sulphuric acid, crystallises from alcohol in yellowish-white needles and melts and decomposes at 239—240°; the *ammonium* salt (anhydrous), the *potassium* salt, with $1H_2O$, and the *sodium* salt, with $\frac{1}{2}H_2O$, form small, yellow needles. The *ethyl* ester crystallises from glacial acetic acid in small, feebly-yellow needles or lustrous leaflets, and melts and decomposes at 227—228°. The *chloride*, *amide*, and *anilide* form small, yellow plates or needles and melt and decompose at 159—160°, 221—222°, and 232—233° respectively.

All attempts to diazotise 1-amino-2-naphthoxyacetic anhydride failed, but on warming with acetic acid and sodium nitrite solution it was converted into 4-*nitro*-1-*amino*-2-*naphthoxyacetic anhydride*,



$NO_2\cdot C_{10}H_5<\begin{array}{l}NH\cdot CO\\ \quad\quad\ \ |\\ O—CH_2\end{array}$, which crystallises in yellow needles and leaflets, commences to decompose at about 290°, and is also obtained by the action of nitric acid on the anhydride; the *sodium* salt,

$$C_{12}H_6O_4N_2Na_2,3H_2O,$$

crystallises in yellow needles and is decomposed by dilute hydrochloric acid to form a red *sodium hydrogen* salt; the *potassium hydrogen* salt, $C_{12}H_7O_4N_2K,1\frac{1}{2}H_2O$, crystallises in reddish-yellow needles.

W. A. D.

Condensation of Benzilic Acid with Phenols. By AUGUSTIN BISTRZYCKI and LEON NOWAKOWSKI (*Ber.*, 1901, **34**, 3063—3073. Compare Abstr., 1897, i, 190).

—p-*Hydroxytriphenylacetic acid*,

$$OH\cdot C_6H_4\cdot CPh_2\cdot CO_2H,$$

prepared by condensing benzilic acid with phenol in the presence of tin tetrachloride, crystallises from dilute alcohol in colourless or pale yellow leaflets melting at 212°, and is readily soluble in all the ordinary organic solvents excepting light petroleum. The *silver* salt is a white, insoluble substance; the other metallic derivatives could not be obtained crystalline. The silver salt does not yield an ester on treatment with methyl iodide; the *dimethyl* ester,

$$OMe\cdot C_6H_4\cdot CPh_2\cdot CO_2Me,$$

is formed, however, on heating a mixture of the acid, methyl iodide, methyl alcohol, and potassium hydroxide at 100°; it crystallises from glacial acetic acid, and melts at 138—139°. This ethereal salt is insoluble in cold dilute potassium hydroxide solution, and is hydrolysed with great difficulty when heated at 100° with this alkali dissolved in methyl alcohol. p-*Methoxytriphenylacetic acid*, $OMe\cdot C_6H_4\cdot CPh_2\cdot CO_2H$, the product of this hydrolysis, crystallises from dilute acetic acid in needles melting at 174°. The *monobromo*-derivative,

$$OMe\cdot C_6H_3Br\cdot CPh_2\cdot CO_2Me,$$

resulting from the action of bromine on the dimethyl ester, crystallises in pale yellow prisms and melts at 126°.

p-*Acetoxytriphenylacetyl acetate*, $OAc\cdot C_6H_4\cdot CPh_2\cdot CO_2Ac$, crystallises in needles melting at 208°; it is not soluble in cold dilute sodium hydroxide solution, but is hydrolysed by a hot concentrated solution of this reagent.

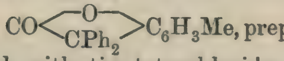
Dibromo-p-*hydroxytriphenylacetic acid*, $OH\cdot C_6H_2Br_2\cdot CPh_2\cdot CO_2H$, produced by brominating the free acid in glacial acetic acid, crystallises in colourless needles and melts at 194—195°.

Dibromo-p-*hydroxytriphenylacetic acetic anhydride*,

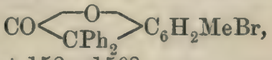
$$OH\cdot C_6H_2Br_2\cdot CPh_2\cdot CO\cdot OAc,$$

formed by the action of acetic anhydride on the preceding compound, crystallises in white needles melting at 212—213°; it is insoluble in cold dilute solutions of the alkalis.

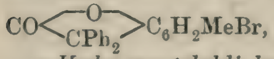
Nitro p-*hydroxytriphenylacetic acid*, $OH\cdot C_6H_3(NO_2)\cdot CPh_2\cdot CO_2H$, obtained by nitrating the acid in glacial acetic acid, crystallises from this solvent in yellow needles melting at 177—178°.

m-*Tolyldiphenylacetic acid lactone*,  $\mathrm{CO}\left\langle\begin{matrix}\mathrm{O}\\ \mathrm{CPh_2}\end{matrix}\right\rangle\mathrm{C_6H_3Me}$, prepared by condensing benzilic acid and *m*-cresol with tin tetrachloride, crystallises in lustrous, snow-white needles melting at 126°; it is insoluble in dilute sodium hydroxide solution, but on boiling with concentrated solutions of the alkali hydroxides it becomes hydrolysed and the product, when acidified, yields the corresponding *acid*,

$$OH\cdot C_6H_3Me\cdot CPh_2\cdot CO_2H;$$

this substance has not, however, been obtained pure, owing to the readiness with which it passes back into the lactone. *Bromo*-m-*tolyldiphenylacetic acid lactone*,  $\mathrm{CO}\left\langle\begin{matrix}\mathrm{O}\\ \mathrm{CPh_2}\end{matrix}\right\rangle\mathrm{C_6H_2MeBr}$, crystallises in colourless plates and melts at 158—159°.

p-*Hydroxy*-m-*tolyldiphenylacetic acid* (4-*hydroxy*-2-*methyltriphenylacetic acid*), $OH\cdot C_6H_3Me\cdot CPh_2\cdot CO_2H$, produced as a bye-product in the preceding condensation, crystallises in colourless needles and melts at 212—213°; its *diacetyl* derivative, $OAc\cdot C_6H_3Me\cdot CPh_2\cdot CO\cdot OAc$, crystallises in aggregates of colourless plates melting at 189°.

p-*Tolyldiphenylacetic acid lactone*, resulting from the condensation of benzilic acid and *p*-cresol, crystallises from alcohol in lustrous, pale yellow prisms melting at 130°; the *acid* is extremely unstable and could not be isolated in a state of purity. The *bromo*-derivative,  $\mathrm{CO}\left\langle\begin{matrix}\mathrm{O}\\ \mathrm{CPh_2}\end{matrix}\right\rangle\mathrm{C_6H_2MeBr}$, melts at 161°.

p-*Hydroxy*-o-*tolyldiphenylacetic acid*, $OH\cdot C_6H_3Me\cdot CPh_2\cdot CO_2H$, prepared from benzilic acid and *o*-cresol, crystallises in colourless plates and melts at 190°; the silver salt is unstable, whilst the green precipitate, produced by adding copper acetate to a solution of the potassium salt, has the composition of a basic salt. G. T. M.

Artemisin. By P. BERTOLO (*Atti Real. Accad. Lincei*, 1901, [v], **10**, ii, 111—116. Compare Merck, Abstr., 1896, i, 59).—Artemisin forms with chloroform a crystalline *compound* of the composition $C_{15}H_{18}O_4,CHCl_3$, the formation of which serves as a convenient means of obtaining pure artemisin, since the whole of the chloroform is evolved at 80°.

The *sodium* salt of artemisin, obtained by treating an aqueous alcoholic solution of artemisin with sodium carbonate, crystallises from alcohol in shining, colourless, flattened needles which effloresce when kept over sulphuric acid; it is very oluble in water, the solution having a bitter, saline taste. Treated with dilute sulphuric acid, it yields artemisin, whilst treatment with concentrated sulphuric acid gives a white *precipitate* which separates from alcohol in large, tabular crystals melting at 170—171°; this substance is to be further investigated. The *silver* salt of artemisin, $C_{15}H_{19}O_5Ag$, separates as a white precipitate.

Artemisin oxime, $C_{15}H_{19}O_4N$, crystallises from methyl alcohol in white, silky needles, which sometimes form star-shaped aggregates and melt at 233—234°; it is slightly soluble in water, readily in alcohol, ether, or chloroform, and dissolves also in cold dilute aqueous alkali hydroxides.

Artemisin apparently forms a hydrazone and an osazone.

T. H. P.

Behaviour of Bromine towards the Unsaturated Condensation Products from Benzyl Cyanide and the Substituted Benzaldehydes. By AUGUSTIN BISTRZYCKI and ERWIN STELLING (*Ber.*, 1901, **34**, 3081—3089. Compare Frost, Abstr., 1889, 597, and Walther and Wetzlich, Abstr., 1900, i, 438).—*a-Phenylbromopiperonylcinnamonitrile*, $C_7H_4O_2Br\cdot CH\colon CPh\cdot CN$, produced by brominating the condensation product of piperonaldehyde and benzyl cyanide in chloroform solution, crystallises in yellow prisms and melts at 179°. *a-Phenyl-*p*-hydroxycinnamonitrile*, $OH\cdot C_6H_4\cdot CH\colon CPh\cdot CN$, obtained by condensing *p*-hydroxybenzaldehyde and benzyl cyanide in an absolute alcoholic solution of sodium ethoxide, crystallises from dilute alcohol in colourless needles melting at 192°; it does not form an additive compound with bromine. A stereoisomeric substance is formed when the reaction is repeated in dilute alcohol; this compound also melts at 190—191°, but differs from its isomeride in being insoluble in chloroform, carbon disulphide, or benzene, whereas the preceding compound is soluble in the organic solvents, excepting light petroleum. The *acetyl* derivative, $OAc\cdot C_6H_4\cdot CH\colon CPh\cdot CN$, forms colourless leaflets and melts at 121—122°.

m-Hydroxybenzaldehyde and benzyl cyanide yield the same product whether they are condensed with sodium ethoxide or hydroxide; this compound, *a-phenyl-*m*-hydroxycinnamonitrile*, crystallises from dilute acetic acid in plates melting at 106—107°; its *acetyl* derivative melts at 75—76°.

The *dibromide*, $C_{15}H_9ONBr_2$, produced in chloroform solution, crystallises in prisms and melts at 182°; this reaction does not take place very readily and the yield of additive product is very small. Vanillin and salicylaldehyde do not interact with benzyl cyanide, whilst cuminaldehyde gives rise to tarry products.

*a-Phenyl-*m*-ethoxycinnamonitrile,* $OEt{\cdot}C_6H_4{\cdot}CH{:}CPh{\cdot}CN$, prepared from *m*-ethoxybenzaldehyde, crystallises from alcohol in aggregated plates and melts at 72°; the *dibromide,* $C_{17}H_{13}ONBr_2$, forms lustrous leaflets or white, felted needles and melts at 119°; its formation is accompanied by a considerable evolution of hydrogen bromide and it is probably a substitution product having one or other of the formulæ $OEt{\cdot}C_6H_2Br_2{\cdot}CH{:}CPh{\cdot}CN$ or $OEt{\cdot}C_6H_3Br{\cdot}CBr{:}CPh{\cdot}CN$.

*a-Phenyl-*o*-ethoxycinnamonitrile,* obtained from the ethyl derivative of salicylaldehyde, crystallises in snow-white needles and melts at 82°. The *tribromide,* $OEt{\cdot}C_6H_4Br{\cdot}CHBr{\cdot}CBrPh{\cdot}CN$, produced from the preceding nitrile and 6 atomic proportions of bromine, crystallises in plates melting at 114° with a liberation of bromine; this behaviour seems to indicate that the substance is a dibromide.

*a-Phenyl-*p*-methoxydibromocinnamonitrile,* $OMe{\cdot}C_6H_2Br_2{\cdot}CH{:}CPh{\cdot}CN$, results from the action of bromine (6 atoms.) on *a-phenyl-*p*-methoxycinnamonitrile,* the action being attended by the liberation of hydrogen bromide; it forms prismatic lamellæ and melts at 186°; the bromine is not removed by heating with sodium ethoxide.

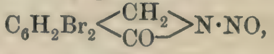
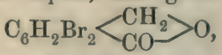
*a-Phenyl-*m*-bromo-*p*-methoxycinnamonitrile,* prepared by condensing *m*-bromoanisaldehyde and benzyl cyanide, crystallises in silky prisms and melts at 102°.

*a-Phenyl-*p*-methylcinnamonitrile,* $C_6H_4Me{\cdot}CH{:}CPh{\cdot}CN$, derived from *p*-tolylaldehyde, crystallises from alcohol either in rhombic or monoclinic prisms, both forms melting at 61°; it absorbs bromine very slowly, yielding tarry products. G. T. M.

Constitution of Dibromophthalic Acid. By O. BRÜCK (*Ber.*, 1901, **34**, 2741—2747).—The dibromophthalic acid described by Juvalta (D.R.-P. 50177) and by Blümlein (Abstr., 1885, 162) is shown by two separate methods to be 4:5-dibromo-1:2-phthalic acid.

Dimethyl 4:5-*dibromophthalate,* $C_6H_2Br_2(CO_2Me)_2$, crystallises from methyl alcohol in colourless needles and melts at 81—83°. The *diethyl* ester, $C_{12}H_{12}O_4Br_2$, crystallises from alcohol in glistening, transparent needles and melts at 63—65°. The *monoethyl* ester, prepared by heating the anhydride with absolute alcohol, forms long needles, melts at 147—149°, and can also be prepared by hydrolysing the diethyl ester with alcoholic potassium hydroxide. The formation of these esters corresponds with the behaviour of a 4:5-acid, but not with that of a 3:4- or 4:6-acid.

By fusing with potassium hydroxide, the acid is converted into a dihydroxyphthalic acid identical with the 4:5-acid described by Rossin (Abstr., 1892, 180) and by Freund (Abstr., 1893, i, 117); the acid, contrary to the description of Rossin and Freund, was observed to melt with formation of the anhydride at 175°, but the identity of the two acids was proved by crystallographic measurements and the constitution of the dibromo-acid was thus established.

4:5-*Dibromophthalimidine,* $C_6H_2Br_2{<}\substack{CH_2\\CO}{>}NH$, prepared by reducing the phthalimide with tin and hydrochloric acid, crystallises from alcohol in glistening, white needles with a greenish shimmer, melts at 279—280° to a turbid red liquid, and has no marked basic properties. The *nitroso*-derivative,  $C_6H_2Br_2<\substack{CH_2\\CO}>N\cdot NO$, crystallises from alcohol in yellow needles, melts at 183—185° to a turbid liquid, and gives Liebermann's reaction. 4 : 5-*Dibromophthalide*,  $C_6H_2Br_2<\substack{CH_2\\CO}>O$, prepared by the action of sodium hydroxide on the nitroso-derivative, sublimes in pure white crystals and melts at 225—227° ; it is reduced by phosphorus and hydriodic acid to the 4 : 5-dibromo-*o*-toluic acid described by Claus and Beck (Abstr., 1892, 1207), thus again establishing the constitution of the dibromophthalic acid.

T. M. L.

Action of Sulphuryl Chloride on Methyl Protocatechuate. Dichloroprotocatechuic Acid and Dichloroveratric Acid.

By Girolamo Mazzara (*Gazzetta*, 1901, **31**, i, 554—560 ; ii, 94—104).—The action of sulphuryl chloride on methyl protocatechuate (methyl 3 : 4-dihydroxybenzoate), gives rise to two isomeric methyl dichloroprotocatechuates, $C_6HCl_2(OH)_2\cdot CO_2Me$, the relations between which are not yet definitely established. One *ester* crystallises from dilute alcohol in almost white needles having a pale rose tint and melting with slight decomposition at 223—225° ; it dissolves slightly in water, the solution giving with ferric salts a chrome-green coloration whilst solutions of the alkali carbonates dissolve the ester with formation of a yellowish-green colour. The other *ester* crystallises from dilute alcohol in long, slender, sparkling needles containing $1H_2O$, whilst when dried it separates from benzene in white needles melting at 105° ; in aqueous solution, it yields an indigo-blue coloration with ferric chloride.

The two methyl dichloroprotocatechuates (*loc. cit.*) form, with ammonium salts, precipitates which are readily decomposed by sodium carbonate solutions and the examination of which is being continued.

Since the two dichloroprotocatechuic acids obtained by hydrolysing the two methyl esters are readily and almost quantitatively esterified by means of alcohol and hydrogen chloride, these esters must have the constitutions $CO_2Me : Cl_2 : (OH)_2 = 1 : 2 : 5 : 3 : 4$ or $1 : 5 : 6 : 3 : 4$; the ester melting at 105°, which crystallises with $1H_2O$, probably has the first of these constitutions.

Dichloroprotocatechuic acid, $C_6HCl_2(OH)_2\cdot CO_2H,3H_2O$, obtained by hydrolysing the methyl ester melting at 105°, crystallises from aqueous alcohol in long, silky prisms ; in aqueous solution, it gives a blue coloration with ferric chloride. The *isomeride* prepared from the methyl ester melting at 223—225° separates from alcohol in sparkling prisms which blacken slightly at 230° and melt and decompose at 239° ; its aqueous solution gives an azure-blue coloration with ferric salts.

Methyl dichloroveratrate, $C_6HCl_2(OMe)_2\cdot CO_2Me$, prepared from the dichloroprotocatechuic acid melting at 239° by heating it with potassium hydroxide and methyl iodide in presence of methyl alcohol, crystallises from aqueous alcohol in small prisms melting at 95—96°.

The corresponding *dichloroveratric acid* is deposited from dilute alcohol in small crystals, which, after drying at 100°, melt at 182—183°; it is slightly soluble in water, its solution giving no coloration with ferric salts, and on esterification the methyl ester is obtained in almost quantitative proportion. T. H. P.

p-Methoxyatrolactic Acid. By J. Bougault (*Bull. Soc. Chim.*, 1901, [iii], **25**, 854—856).—p-*Methoxyatrolactic acid*,

$$OMe\cdot C_6H_4\cdot CMe(OH)\cdot CO_2H,$$

best obtained by the oxidation of *p*-methoxyhydratropic acid (Abstr., 1901, i, 548) in the cold with a large excess of potassium permanganate, is a crystalline substance melting at 129—130° and is optically active. The action of hydriodic acid converts it into *p*-hydroxyhydratropic acid. The sodium and calcium salts crystallise with $2H_2O$. N. L.

3 : 4-Dioxymethylenehydratropic Aldehyde and Acid. By J. Bougault (*Bull. Soc. Chim.*, 1901, [iii], **25**, 856—858. Compare Abstr., 1900, i, 495).—3 : 4-*Methylenedioxyhydratropaldehyde*,

$$CH_2{:}O_2{:}C_6H_3\cdot CHMe\cdot CHO,$$

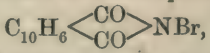
obtained by oxidising *iso*safrole in ethereal solution with a mixture of mercuric oxide and iodine, is a colourless, highly refracting liquid which boils at 279—280°, and has a sp. gr. 1·203 at 15°; the *oxime* melts at 71°. Chromic acid oxidises the aldehyde to 3 : 4-methylenedioxyacetophenone, whilst potassium permanganate in alkaline solution converts it into 3 : 4-methylenedioxyphenylglyoxylic acid and finally into piperonic acid.

3 : 4-*Methylenedioxyhydratropic acid*, $CH_2{:}O_2{:}C_6H_3\cdot CHMe\cdot CO_2H$, obtained by oxidising the corresponding aldehyde with silver oxide in alkaline solution, forms anhydrous, prismatic crystals melting at 80°. Chromic acid oxidises it to the ketone, $CH_2{:}O_2{:}C_6H_3\cdot COMe$, and potassium permanganate to piperonic acid. By repeated crystallisation of its morphine salt, the acid may be resolved into two optically active components. The *sodium*, *calcium* (with $2H_2O$), *copper*, and *silver* salts have been prepared. N. L.

Naphthalic Acid and Naphthalimide. By Luigi Francesconi and V. Recchi (*Atti Real. Accad. Lincei*, 1901, [v], **10**, ii, 85—93).—In order to follow up the analogies observed in the behaviour of phthalic and 1 : 8-naphthalic acid, the authors have studied the reactions of the latter acid with antimony pentachloride and of the amide of this acid with alkali hypobromite and hypochlorite.

By heating 1 : 8-naphthalic anhydride with antimony pentachloride at 180° and afterwards passing chlorine into the mixture, two compounds are obtained: (1) *Hexachloronaphthalic anhydride*, $C_{12}O_3Cl_6$, which crystallises from acetic acid in lustrous, pale yellow plates melting at 205°; it is soluble in ethyl acetate or acetone, and slightly so in alcohol. With resorcinol, it condenses, giving a fluorescent solution which is green by reflected, and yellowish-red by transmitted light. Sulphuric acid does not give the azure fluorescence which it does with tetrachlorophthalic anhydride. It is slightly soluble in concentrated sodium carbonate solution, from which mineral acids precipitate *hexachloronaphthalic acid* in the form of white flocks; this, when boiled with alcohol, is reconverted into the anhydride. (2) A *carbon chloride* of the composition $C_{12}Cl_{14}$, which, when slowly deposited from ether, is obtained in crystals resembling cubes, whilst rapid crystallisation yields acicular crystals; from alcohol, both forms are simultaneously deposited. The crystals melt at 135—136° and are triclinic: [$a:b:c = 0{\cdot}73660:1:0{\cdot}93952$. $\alpha = 99°30'$; $\beta = 88°7'$; $\gamma = 118°22'$]. A monoclinic form was also observed, but was not obtained in a stable condition. It is extremely soluble in benzene, less so in ether or ethyl acetate, and to a slight extent in alcohol or acetic acid. The values found for its molecular weight are 435—471 in freezing benzene; 530 and 541 in boiling acetic acid; 529—551 in boiling benzene, and 634 and 670 in boiling alcohol, the calculated value being 639. It resists energetically the action of oxidising agents, being unaltered by boiling with sulphuric acid and dichromate in acetic acid solution, but alkalis in alcoholic solution convert it into a brown, uncrystallisable resin. Zinc and acetic acid act on it, yielding a *reduction product* which is slightly soluble in alcohol or ether, giving solutions coloured violet by light; it dissolves in ethyl acetate, acetic acid, or benzene, crystallising from the last-named in lustrous prisms which melt at 225° and on further heating evolve chlorine.

The action of phosphorus pentachloride on 1 : 8-naphthalic anhydride yields an unstable naphthalyl chloride, which could not be isolated as it rapidly absorbs water from the air, being converted into naphthalic anhydride and hydrochloric acid; this instability indicates a symmetrical constitution for the chloride.

The action of potassium hypobromite on 1 : 8-naphthalimide in the cold yields 1 : 8-*naphthalbromoimide*,  $C_{10}H_6{<}^{CO}_{CO}{>}NBr$, which crystallises from benzene in lustrous, yellow laminæ decomposing at about 200°. It did not give satisfactory numbers on analysis, as it is readily converted into naphthalimide by water or alkalis.

1 : 8-*Naphthalchloroimide*, $C_{12}H_6O_2NCl$, obtained similarly to the bromo-compound, crystallises from benzene in lustrous, white plates which melt at 233—234° and are soluble in ethyl acetate, alcohol, or chloroform. By ammonia or amines, it is reconverted into naphthalimide. When treated with hot potassium hypobromite, naphthalimide is converted in small quantity into 1 : 8-aminonaphthoic acid. T. H. P.

Action of Sulphuryl Chloride on the Methyl and Ethyl Esters of Gallic Acid. By GIROLAMO MAZZARA and P. GUARNIERI (*Gazzetta*, 1901, **31**, ii, 184—190. Compare Abstr., this vol., i, 594).—*Methyl dichlorogallate*, $C_6Cl_2(OH)_3{\cdot}CO_2Me$, obtained by the action of 2 mols. of sulphuryl chloride on methyl gallate, crystallises from water in monoclinic, prismatic plates which contain $1\frac{1}{2}H_2O$, and, when dehydrated, melt at 169—170°; it is soluble in solutions of the alkali carbonates, to which it imparts a red colour, whilst with ferric chloride solution it gives an azure coloration.

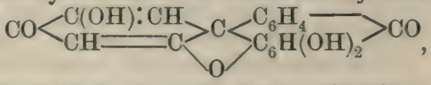
Ethyl chlorogallate, $C_6HCl(OH)_3{\cdot}CO_2Et$, crystallises from water in mammillary masses of thin needles containing $1H_2O$; with alkali carbonates, it gives a yellowish, and with ferric salts an azure, coloration. The anhydrous ester melts at 106—107°.

Methyl chlorogallate, $C_6HCl(OH)_3{\cdot}CO_2Me$, separates from water in yellow prisms containing $1H_2O$, the anhydrous salt melting at 159—160°.

These results show that those monochloro-derivatives of the esters of gallic acid which have the halogen atom between the CO_2R group and hydroxyl crystallise with $1H_2O$, whilst the dichloro-compounds contain $1\frac{1}{2}H_2O$. Also, the methyl derivatives melt at a higher temperature than the corresponding ethyl compounds. T. H. P.

Dihydroxyfluorescein. By JOHANNES THIELE and CARL JAEGER (*Ber.*, 1901, **34**, 2617—2620).—Dihydroxyfluorescein has already been described by Liebermann (Abstr., 1901, i, 595). The *ammonium* salt, $C_{20}H_{12}O_7\cdot NH_3$, is a dark green mass, which is formed by the action of gaseous ammonia on air-dried dihydroxyfluorescein and forms a reddish-brown solution in water, exhibiting a dark-green fluorescence.

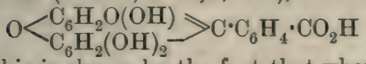
Dibromodihydroxyfluorescein, $C_{20}H_{10}O_7Br_2$, is a red powder which decomposes above 200°. Dihydroxyfluorescein is converted by sulphuric acid at 120° into *violein*,



$$CO\Big<\begin{array}{l}C(OH){:}CH\\CH{=\!=\!=}C\end{array}\Big>C\Big<\begin{array}{l}C_6H_4\text{———}\\C_6H(OH)_2\end{array}\Big>CO,\quad \text{(C and }C_6H(OH)_2\text{ bridged by O)}$$

which is a dark powder forming violet-coloured solutions in nitrobenzene, aniline, or acetic acid, and deep blue salts with alkalis. The *triacetate* is a dark brownish, violet powder. A. H.

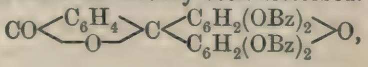
The Phthalein of Hydroxyquinol. By W. FEUERSTEIN and M. DUTOIT (*Ber.*, 1901, **34**, 2637—2642).—Hydroxyquinolphthalein (dihydroxyfluorescein), which has been previously described by Liebermann (Abstr., 1901, i, 595), has the constitution



$$O\Big<\begin{array}{l}C_6H_2O(OH)\\C_6H_2(OH)_2\end{array}\Big>C\cdot C_6H_4\cdot CO_2H\ [O:(OH)_3:CO_2H=3:2:6:7:2'].$$

This is shown by the fact that when treated with alcohol and sulphuric acid it yields an *ethyl ester*, $C_{19}H_8O_2(OH)_3\cdot CO_2Et$, which crystallises in green plates melting at 326°. This ester has almost the same tinctorial properties as the original colouring matter, which shows that the two substances must be similarly constituted. The ester yields a *triacetyl* derivative, which forms hard, orange-yellow crystals, melts at 238—239°, and shows an intense fluorescence in dilute solution.

On the other hand, the action of acid chlorides on the phthalein brings about a molecular rearrangement and colourless substances are produced. Of these the tetra-acetyl derivative has already been described. *Tetrabenzoylhydroxyquinolphthalein*,



$$CO\Big<\begin{array}{c}C_6H_4\\O\end{array}\Big>C\Big<\begin{array}{l}C_6H_2(OBz)_2\\C_6H_2(OBz)_2\end{array}\Big>O,$$

forms large, compact crystals.

[W. FEUERSTEIN and JEAN WALLACH].—Fluorescein itself may readily be esterified directly by the action of alcohol and sulphuric acid. The ethyl ester prepared in this way is a red powder melting at 242°, whilst that obtained indirectly by Nietzki and Schröter (Abstr., 1895, i, 183) is described as melting at 247°. On treatment with acetic anhydride, it yields *monoacetylfluorescein ethyl ester*, $C_{24}H_{18}O_6$, crystallising in orange-coloured needles, which have a blue surface lustre and melt at 191°. *Fluorescein methyl ester* forms red crystals with a green lustre and melts at 252—253°. A. H.

Constitution of Gallein and Cœrulein. By WILLIAM R. ORNDORFF and C. E. BREWER (*Amer. Chem. J.*, 1901, **26**, 97—158. Compare Abstr., 1900, i, 447; Buchka, Abstr., 1882, 58; Herzig, Abstr., 1892, 1319).—Gallein tetra-acetate melts at 241° (Buchka gives 247—248° and Herzig 236—237°); it separates from a mixture of alcohol and chloroform in triclinic crystals, of which measurements are given. The tetrabenzoate melts at 226° (Buchka gives 231°), but it was not found possible to estimate the number of benzoyl groups by hydrolysis. Gallin tetra-acetate is an acid and the *silver* salt, $C_{20}H_9O_7Ac_4Ag$, was obtained as a white precipitate resembling silver chloride.

Gallein methyl ester, $C_{19}H_8O_2(OH)_3\cdot CO_2Me$, separates from ether in dark red, granular masses with a bronze-like lustre and does not melt at 280°; the *ethyl ester* forms crystals which are red by transmitted, and green by reflected, light.

Gallein triphenylcarbamate, $C_{20}H_9O_7(CO\cdot NHPh)_3$, is a light yellow solid which does not melt sharply on account of decomposition.

The basic *lead* salt, $C_{20}H_8O_7(Pb\cdot OH)_4$, is a dark blue powder and its formation can be used as a test either for lead or for gallein. The *trimethyl* ether, $C_{20}H_9O_4(OMe)_3$, forms colourless crystals, melts at 229°, and resembles phenolphthalein; the *acetate*, $C_{20}H_8O_3(OMe)_3\cdot OAc$, crystallises from alcohol in needles and melts at 97°. *Gallein tetramethyl ether*, $C_{20}H_8O_3(OMe)_4$, exists in two modifications; the *coloured* ether forms dark red, monoclinic pyramids, melts sharply at 199°, and is readily hydrolysed by alcoholic sodium carbonate to the colourless trimethyl ether; the *colourless* ether crystallises in needles, melts at 195°, is less soluble in organic solvents than the coloured ether, and is insoluble in aqueous potassium hydroxide, even on boiling. The *coloured tetraethyl ether*, $C_{20}H_8O_3(OEt)_4$, forms dark red, monoclinic crystals and melts at 155°; it is readily hydrolysed to the colourless *triethyl ether*; the *colourless tetraethyl ether* crystallises from alcohol in needles, melts at 144°, and is insoluble in boiling aqueous alkalis.

Gallin pentamethyl ether, $C_{20}H_9O_2(OMe)_5$, separates from alcohol and acetic acid in crystals which are almost white and melts at 127°.

Cœrulein triacetate was prepared by Buchka's method and the number of acetyl groups determined by hydrolysis. The acetate of cœrulin was also prepared by Buchka's method, but hydrolysis showed it to be a *penta acetate* and not a tetra-acetate; it was also found not to melt at 256°, but to decompose without melting. Cœrulein forms two *monomethyl* ethers; one separates from alcohol in dark crystals with a bronze-like lustre, decomposes without melting when heated, and dissolves to an olive-brown solution in alcohol, acetone, pyridine, aniline, or potassium hydroxide; the other is more soluble and dissolves in acetone or pyridine with a purple colour, in alcohol or aniline with a greenish-blue colour, and in aqueous potassium hydroxide with a light green colour. The *monoethyl* ether was also prepared.

T. M. L.

Caffetannic Acid. By CARL RUNDQVIST (*Chem. Centr.*, 1901, ii, 773—774; from *Pharm. Post.*, **34**, 425—426).—Domingo and Guatemala coffee contain 5·928 and 6·292 per cent. of sucrose respectively. The magnesium and calcium salts of caffetannic acid can be extracted from coffee by means of absolute methyl alcohol and are precipitated from the solution on the addition of ether. The free acid forms a pale yellow, flexible, transparent mass which does not attain a constant weight when allowed to remain over phosphoric oxide in a vacuum. The *hexa-acetyl* derivative, $C_{34}H_{32}O_{13}Ac_6$, forms a dusty, grey, amorphous powder which is not affected by exposure to the atmosphere, melts and decomposes at 94°, and is readily soluble in hot alcohol, acetone, or chloroform, slightly so in cold alcohol, and insoluble in water or ether. On rubbing, the powder becomes strongly electrified and when suspended in water it combines with a considerable quantity of bromine. By the action of a 5 per cent. solution of sulphuric acid on caffetannic acid, caffeic acid is formed, but since no sugar is obtained the acid cannot be regarded as a glucoside acid.

E. W. W.

Benzaldehyde-*o*-sulphonic Acid. LEVINSTEIN (LIMITED) (D.R.-P. 119163. Compare D.R.-P. 115410).—*Benzaldehyde-o-sulphonic acid* is prepared by oxidising calcium stilbene-*o*-disulphonate in aqueous solution with potassium permanganate; it yields on condensation with dimethylaniline a sulphonated leuco-base giving rise to a greenish-blue colouring matter identical with that described in D.R.-P. 89397. The stilbenesulphonic acid employed in this preparation is obtained from diaminostilbenedisulphonic acid (compare Bender and Schultz, Abstr., 1887, 268).

G. T. M.

Preparation of 2:5-Dimethylbenzaldehyde; the Establishment of its Constitution and Preparation of some of its Derivatives. By EVERHART P. HARDING and LILLIAN COHEN (*J. Amer. Chem. Soc.*, 1901, **23**, 594—606).—An investigation as to whether, in the preparation of aldehydes by the method of Gattermann and Koch (Abstr., 1897, i, 519), the aldehyde group can enter the benzene ring without occupying the para-position to a methyl group.

2:5-*Dimethylbenzaldehyde*, $C_6H_3Me_2{\cdot}CHO$, prepared by the above method, is a colourless liquid which boils at 219—229° (uncorr.), has the odour of benzaldehyde, and is soluble in all the usual solvents except water; on exposure to the air, it is rapidly oxidised and becomes yellow. The *aldazine*, $C_6H_3Me_2{\cdot}CH{:}N{\cdot}N{:}CH{\cdot}C_6H_3Me_2$, forms yellow crystals, melts at 114—114·5°, and is soluble in alcohol, ether, benzene, or glacial acetic acid. The *phenylhydrazone* is obtained as a yellowish-white precipitate; when crystallised from glacial acetic acid, it melts at 84—85·5°, and is soluble in alcohol, ether, or benzene; it is unstable and rapidly darkens in colour. The *oxime* forms colourless crystals, melts at 83·5—84°, and is soluble in alcohol, ether, benzene, or acetic acid. The *benzidine* derivative forms sulphur-yellow, rhombic crystals [$a:b:c = 0{\cdot}5255+ : 1 :$ approx. $1+$], melts at 187·5° (uncorr.), and is soluble in benzene or chloroform. The *aniline* derivative crystallises in lustrous plates, melts at 51° (uncorr.), and is readily soluble in alcohol, benzene, or light petroleum; it is decomposed by water with regeneration of aniline and the aldehyde.

2:5-*Dimethylbenzoic acid*, $C_6H_3Me_2{\cdot}CO_2H$, obtained by shaking the aldehyde with strong solution of sodium hydroxide, crystallises in colourless needles of the mono- or tri-clinic system [$\beta = 58°21'$], melts at 124—125° (uncorr.), and is soluble in alcohol, benzene, chloroform, or acetone.

2 : 5-*Dimethylcinnamic acid*, $C_6H_3Me_2{\cdot}CH{:}CH{\cdot}CO_2H$, obtained by the action of malonic acid on the aniline derivative of dimethylbenzaldehyde, crystallises in white, triclinic needles, melts at 176·5° (uncorr.), and is soluble in alcohol, ether, chloroform, benzene, light petroleum, acetone, or hot water. On reduction with sodium amalgam, it is converted into 2 : 5-*dimethylhydrocinnamic* [*β*-2 : 5-*xylylpropionic*] *acid*, $C_6H_3Me_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, which crystallises in needles and melts at 111·5° (uncorr.).

By the action of hydrogen sulphide on an alcoholic solution of dimethylbenzaldehyde, the *trithio*-derivative, $(C_6H_3Me_2{\cdot}CHS)_3$, is produced, which crystallises in large, colourless, monoclinic plates, melts at 110° (uncorr.), and is soluble in benzene, alcohol, or chloroform.

E. G.

Synthesis of Aromatic Alcohols by means of Formaldehyde.

By Richard Stoermer and K. Behn (*Ber.*, 1901, **34**, 2455—2460).—The presence of a negative group (CHO, NO_2, CO_2H, Cl) in the ortho-position relatively to the hydroxyl of phenols causes the latter to condense with formaldehyde in hydrochloric acid solution to form hydroxybenzyl alcohols containing the methylol group in the para-position with regard to the hydroxyl radicle.

2-*Hydroxy*-5-*methylolbenzaldehyde*, obtained from salicylaldehyde, crystallises from water in long, white needles, melts at 108°, and does not reduce solutions of silver or Fehling's solution; hydrogen chloride in absolute alcoholic solution converts it into the chloride

$$CHO{\cdot}C_6H_3(OH){\cdot}CH_2Cl$$

(German Patent 114194). The latter is probably the first product of the interaction between formaldehyde and salicylaldehyde in presence of hydrogen chloride, as on pouring off the formaldehyde solution and removing the excess of salicylaldehyde with steam, an oil remains from which water does not extract hydroxymethylol benzaldehyde; the oil is probably the *ether*, $O[CH_2{\cdot}C_6H_3(OH){\cdot}CHO]_2$, as it is converted by alcoholic hydrogen chloride into the chloride described in the German patent. The *azine*,

$$N_2[{:}CH{\cdot}C_6H_3(OH){\cdot}CH_2{\cdot}OH]_2,$$

is a yellowish-white, crystalline powder melting at 219°; the *phenylhydrazone* is similar and melts at 142°. On methylating the aldehyde-alcohol with methyl iodide, a mixture of the phenolic and alcoholic ethers is obtained, which on oxidation with alkaline potassium permanganate yields 4-methoxy*iso*phthalic acid.

From 2-hydroxy-*m*-tolualdehyde, the *compound* $C_9H_{10}O_3$ is obtained, which crystallises from light petroleum in yellowish needles, melts at 83°, and yields a *chloride*, $C_9H_9O_2Cl$, crystallising from the same solvent in long, white, silky needles and melting at 82°.

3-*Nitro*-4-*hydroxybenzyl alcohol*, obtained from *o*-nitrophenol, crystallises from water in long, yellow needles, melts at 97°, and yields a *chloride*, $C_7H_6O_3NCl$, crystallising from light petroleum in long leaflets and melting at 72°; the *methyl* ether of the alcohol separates from water in bright yellow needles, melts at 69°, and on oxidation with potassium permanganate yields 3-nitro-4-methoxybenzoic acid.

The *benzyl alcohol* obtained from *o*-chlorophenol crystallises from benzene in small, white needles, melts at 123°, and yields a *chloride* melting at 93°.

W. A. D.

Halogen-Methyl Derivatives of the Aromatic Aldehydes. Farbenfabriken vorm. F. Bayer & Co. (D.R.-P. 120374. Compare D.R.-P. 114194).—Derivatives of the aromatic hydroxyaldehydes containing the radicle $\mathrm{CH_2X}$ (X = a halogen) are obtained by the interaction of these aldehydes with chloro- or bromo-methyl alcohol, the reaction taking place more readily in the presence of a condensing agent such as zinc chloride, phosphorus oxychloride, or phosphoric oxide than in that of a mineral acid.

2-Hydroxy-5-bromomethylbenzaldehyde, $\mathrm{CH_2Br{\cdot}C_6H_3(OH){\cdot}CHO}$ (m. p. 106°), is produced by the interaction of salicylaldehyde and bromomethyl alcohol in glacial acetic acid containing zinc chloride.

Chloromethylvanillin, prepared by condensing vanillin and chloromethyl alcohol with phosphorus oxychloride, crystallises in colourless leaflets and melts at 127°. *Iodomethyl vanillin,* produced in a similar manner, separates from glacial acetic acid in yellow crystals melting at 157—158°.

G. T. M.

Isolation of *iso*Irone from Bearswort Oil. Haarmann & Reimer (D.R.-P. 120559).—*iso*Irone, $\mathrm{C_{13}H_{20}O}$, is obtained from bearswort oil ("Kostuswurzelöl") by treating it with phenylhydrazine-*p*-sulphonic acid in the presence of sodium carbonate, distilling the acidified hydrazonesulphonic acid solution in a current of steam, and rectifying the oil under diminished pressure. The new ketone boils at 140—150° under 20 mm. pressure, and has a sp. gr. 0·93 at 20°; it yields a *p*-bromophenylhydrazone melting at 161—163°; the corresponding irone derivative melts at 168—170°. *iso*Irone, on treatment with dilute hydriodic acid, yields a hydrocarbon which, when subsequently oxidised with potassium permanganate, furnishes the acid $\mathrm{C_{12}H_{12}O_6}$ (m. p. 214°), also produced in a similar manner from irone.

G. T. M.

Ianthone; a Condensation Product of Mesityl Oxide and Lippial or Citral. Durand, Huguenin & Co. and Philippe Barbier (D.R.-P. 118288).—*βζμ-Trimethyltriskaideka-βζθλ-tetrene-κ-one,*

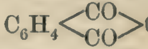
$$\mathrm{CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH{:}CH{\cdot}CO{\cdot}CH{:}CMe_2},$$

results from the condensation of citral or lippial [the lemonal from the essential oil of *Lippia citriodora* (compare Barbier, Abstr., 1899, i, 769)] with mesityl oxide in an aqueous or alcoholic solution of an alkali hydroxide or a salt having an alkaline reaction; it is a yellow oil having no characteristic odour and boils at 185° under 10 mm. pressure.

Ianthone, produced by warming the preceding substance with 60—70 per cent. sulphuric acid, is an isomeric ketone derived from tetrahydrobenzene and having two double linkings in its ketonic side chain; it is a golden-yellow oil soluble in all proportions in the alcohols, and has a characteristic odour of violets. It boils at 162°

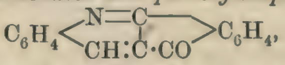
under 10 mm. pressure, and has a sp. gr. 0·9452 at 20°. Ionone is also formed in the preceding transformation, but is readily removed by means of phenylhydrazinesulphonic acid (compare D.R.-P. 73089 and 75120). G. T. M.

Preparation of Anthraphenone. By Eduard Lippmann and Isidor Pollak (*Ber.*, 1901, **34**, 2766. Compare this vol., i, 37).—A solution of anthracene and benzoyl chloride in carbon disulphide, to which zinc dust has been added, is boiled for about three weeks, until hydrogen chloride ceases to be evolved. After removal of the carbon disulphide by distillation, the product is freed from benzoyl chloride by means of sodium hydroxide, dried on a porous plate, and recrystallised from xylene. The yield of anthraphenone is 78 per cent. of the calculated amount. K. J. P. O.

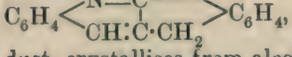
Derivatives of Diketohydrindene (Indanedione). By Emilio Noelting and H. Blum (*Ber.*, 1901, **34**, 2467—2471).—p-*Dimethylaminobenzylideneindanedione*,  $C_6H_4<\begin{smallmatrix}CO\\CO\end{smallmatrix}>C{:}CH\cdot C_6H_4\cdot NMe_2$, obtained by condensing diketohydrindene with *p*-dimethylaminobenzaldehyde in alcoholic solution, crystallises from alcohol in steel-blue crystals, from benzene in scarlet masses, and melts at 99°; the *hydrochloride* is a greyish powder and is decomposed by moisture.

p-*Aminobenzylideneindanedione*, from *p*-aminobenzaldehyde, crystallises from alcohol in blue, lustrous leaflets and melts and decomposes at 247°. 3-*Nitro*-4 *dimethylaminobenzylideneindanedione* crystallises from alcohol in golden-yellow needles and melts at 221°.

On heating *o*-aminobenzaldehyde with diketohydrindene at 100°, 2 mols. of water are eliminated and *quinolylenephenylene ketone*,



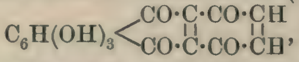
$$C_6H_4<\begin{matrix}N{=}C\\CH{:}\overset{|}{C}\cdot CO\end{matrix}>C_6H_4,$$

is formed; it crystallises from alcohol, melts at 175·5°, and is slightly basic, dissolving to some extent in dilute hydrochloric acid. The *oxime*, $C_{16}H_{10}ON_2$, crystallises from alcohol in small, felted needles and melts and decomposes at 261°; the *phenylhydrazone* crystallises in beautiful, golden-yellow needles and melts at 183°; the *nitrophenylhydrazone* separates from glacial acetic acid as an orange, crystalline mass melting at 256°. *Quinolylenephenylenemethane*,  $C_6H_4<\begin{matrix}N{=}C\\CH{:}\overset{|}{C}\cdot CH_2\end{matrix}>C_6H_4$, obtained by distilling the ketone with zinc dust, crystallises from alcohol, melts at 166—167°, and on distillation with litharge yields a red *hydrocarbon* analogous to that obtained by Graebe by the similar treatment of fluorene. W. A. D.

Preparation of Quinone and Quinol. Theodor Kempf (D.R.-P. 117251).—Benzene is readily oxidised to benzoquinone when suspended in 10 per cent. sulphuric acid in an anode cell furnished with a revolving leaden electrode coated with lead peroxide. The benzene is maintained in an emulsified condition by constant agitation and the mixture is subsequently transferred to the cathode cell where the benzoquinone is reduced to quinol (compare Gattermann and Friedrichs, Abstr., 1894, i, 501). G. T. M.

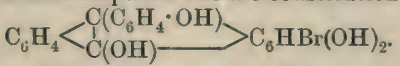
$\Delta^{1,4}$-Terpadiene-3-oxime-6-one (Nitrosothymol). By EDWARD KREMERS and I. W. BRANDEL (*Pharm. Arch.*, 1901, **4**, 107—115).—Goldschmidt and Schmid (Abstr., 1884, 1327) have shown that nitrosothymol is identical with thymoquinoneoxime. The author considers that by the action of nitrous acid on thymol a true nitroso-derivative is probably first formed and that this compound is unstable and readily converted into the oxime, or, possibly, a bisnitroso-derivative. The hydrolysis of nitrosothymol, with formation of thymoquinone, can be effected by heating it with syrupy phosphoric acid for several hours.

E. G.

Transformation of Anthradiquinones and Anthradiquinoneimides into Hydroxyanthraquinones and Aminohydroxyanthraquinones. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 119756).—Pentacyaninequinone,  $C_6H(OH)_3{<}\begin{matrix}CO\cdot C\cdot CO\cdot CH\\ \Vert \qquad \Vert\\ CO\cdot C\cdot CO\cdot CH\end{matrix}$, when dissolved in concentrated sulphuric acid and treated with crystallised boric acid, yields 1 : 3 : 4 : 5 : 7 : 8-hexahydroxyanthraquinone. Under these conditions, the quinoneimides of diaminoanthrarufindisulphonic acid and diaminochrysazindisulphonic acid yield respectively 4 : 8-diaminoanthrachrysone-2 : 6-disulphonic acid and 1 : 8-diamino-2 : 4 : 5 : 7-tetrahydroxyanthraquinone-3 : 6-disulphonic acid.

G. T. M.

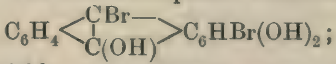
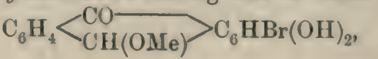
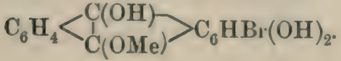
Colouring Matters of the Phenylanthracene Series. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 117894. Compare D.R.-P. 109344 and following abstract).—Chloro- and bromo-deoxyalizarin, when condensed with the phenols, yield a series of colouring matters sparingly soluble in water, but dissolving readily in alkali solutions and the ordinary organic solvents. The condensation product with phenol and the bromo-compound has the constitution



$$C_6H_4{<}\begin{matrix}C(C_6H_4\cdot OH)\\ |\\ C(OH)\text{———}\end{matrix}{>}C_6HBr(OH)_2.$$

Similar substances have been obtained from resorcinol, pyrogallol, salicylic acid, and β-naphthol. Bromodeoxyanthrapurpurin reacts in a similar manner with phenol.

G. T. M.

Preparation of Anthracene Derivatives containing a Halogen Radicle in the Meso-Ring. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 117923. Compare Romer, Abstr., 1881, 823).—Deoxyalizarin and its homologues *deoxyanthrapurpurin* and *deoxyflavopurpurin*, when treated with chlorine or bromine in an indifferent solvent, yield compounds containing one of the meso-hydroxyl groups replaced by the halogen. The bromo-compound obtained from deoxyalizarin has the formula  $C_6H_4{<}\begin{matrix}CBr\text{—}\\ |\\ C(OH)\end{matrix}{>}C_6HBr(OH)_2$; it is a very reactive substance and yields bromoalizarin when warmed with sodium hydroxide. On treatment with methyl alcohol, the compound loses bromine and yields a *methoxy*-derivative having one or other of the following constitutions,  $C_6H_4{<}\begin{matrix}CO\text{———}\\ CH(OMe)\end{matrix}{>}C_6HBr(OH)_2$, or  $C_6H_4{<}\begin{matrix}C(OH)\text{—}\\ |\\ C(OMe)\end{matrix}{>}C_6HBr(OH)_2$.

G. T. M.

Auto-oxidation Products of Anthragallol. I. By MAX BAMBERGER and ARTHUR PRAETORIUS (*Monatsh.*, 1901, 22, 587—589).—Anthragallol was oxidised by drawing air through a strongly alkaline solution for a considerable time. After acidifying, the presence of hydrogen peroxide was demonstrated in the dark coloured solution. On extracting with ether, a sulphur-yellow *compound*, $C_{12}H_{10}O_5$, was obtained, crystallising in plates, melting at 197°, and dissolving in alkalis with a blood-red colour. The *silver* salt, $C_{12}H_8O_5Ag_2$, prepared by boiling an aqueous solution of the compound with silver carbonate, crystallises in violet-red needles. A *methyl* derivative, $C_{12}H_9O_5Me$, prepared by the action of methyl sulphate on a solution of the compound in dilute potassium hydroxide, crystallises in yellow needles melting at 135° and soluble in alkalis. K. J. P. O.

Anthrapurpurin Diacetate. KNOLL & CO. (D.R.-P. 117730).—*Anthrapurpurin diacetate*, prepared by acetylating anthrapurpurin with an equal weight of acetic anhydride or chloride, or with glacial acetic acid and phosphorus oxychloride, is a greenish-yellow powder melting at 175—178°; it is hydrolysed by alkali hydroxides or carbonates and also by the juices of the intestine. G. T. M.

Constitution of Citronellaldehyde. By CARL D. HARRIES and OTTO SCHAUWECKER (*Ber.*, 1901, 34, 2981—2991. Compare this vol., i, 448).—*Dihydroxydihydrocitronellaldimethylacetal*,

$$OH\cdot CH_2\cdot CMe(OH)\cdot[CH_2]_3\cdot CHMe\cdot CH_2\cdot CH(OMe)_2,$$

produced by oxidising citronellaldimethylacetal with potassium permanganate in dilute acetone solution (Sachs, this vol., i, 272), is an oil boiling at 151—153° under 9 mm. pressure and having a sp. gr. 1·0053 at 11°; it does not reduce Fehling's solution even on warming. The *dihydroxyaldehyde*, obtained by boiling the preceding compound with dilute hydrochloric acid, is an unstable oil boiling at 158—162° under 22 mm. pressure; it has a pungent odour and reduces Fehling's solution on warming. The alternative formula,

$$OH\cdot CMe_2\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH(OMe)_2,$$

for the preceding glycol-acetal is excluded by the fact that on oxidation with 1 or 3 atomic proportions of oxygen derived from chromic acid, it yields respectively, either the *dialdehyde*,

$$CHO\cdot CMe(OH)\cdot[CH_2]_3\cdot CHMe\cdot CH_2\cdot CHO,$$

a viscid, colourless oil boiling at 138—140° under 10 mm. pressure, or the *ketoaldehyde* (3-methyloctanone-7-al), a yellow liquid boiling at 115—118° under 16—17 mm. pressure. These compounds have aldehydic odours and properties; they reduce Fehling's solution and develop a coloration with rosaniline sulphite; the dialdehyde also polymerises under the influence of mineral acids or alkalis. Both substances give rise to oily phenyl- and *p*-bromophenyl-hydrazones, but the ketoaldehyde yields a crystalline disemicarbazone forming white leaflets and melting at 244—245°, whilst that from the dialdehyde is oily. The *acetal*, $COMe\cdot[CH_2]_3\cdot CHMe\cdot CH_2\cdot CH(OMe)_2$, of the ketoaldehyde, an oil boiling at 130—135° under 14 mm. pressure, is formed in small amount during the preparation of the aldehyde; it yields an oily phenylhydrazone, but does not reduce Fehling's solution. G. T. M.

Constitution of Licareol (Linalool). By PHILIPPE BARBIER (*Bull. Soc. Chim.*, 1901, [iii], **25**, 828—832).—It has been shown in a previous paper (this vol., i, 477) that the formula,

$$CMe_2\colon CH\cdot CH_2\cdot CH_2\cdot CMe(OH)\cdot CH\colon CH_2,$$

formerly assigned to licareol, belongs in reality to myrcenol, and it is now suggested that licareol has the constitution

$$CMe_2\colon CH\cdot CH_2\cdot CH_2\cdot CMe\colon CH\cdot CH_2\cdot OH,$$

and is stereoisomeric with lemonol. The oxidation products of licareol are identical with those of lemonol, and it is shown that all the reactions of licareol are simply explained by the formula proposed. The experiments of the author and others point to the conclusion that pure licareol would be found to be optically inactive, a result which is in accordance with the new, but not with the old, formula. N. L.

Chloromethyl Menthyl Oxide. EDGAR WEDEKIND (D.R.-P. 119008).—*Chloromethyl menthyl oxide*, $C_{10}H_{19}O\cdot CH_2Cl$, prepared by saturating a mixture of menthol and formalin solution with hydrogen chloride at the temperature of the water-bath, is a colourless, highly refractive oil boiling at 160—163° under 13—16 mm. pressure; it has $[\alpha]_D$ $-172{\cdot}57°$ at 27° and a sp. gr. 0·9821 at 4°. This ether is very easily resolved into menthol, formaldehyde, and hydrogen chloride by the action of water, and undergoes partial decomposition when distilled under reduced pressure, yielding methylenedimenthyl ether, $C_{21}H_{40}O_2$.
G. T. M.

βζ-Dimethyl-βε-octadiene-θ-al, an Isomeride of Citral. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 118351).—ζζ-Dichloro-β-methylheptene, $CMe_2\colon CH\cdot CH_2\cdot CH_2\cdot CMeCl_2$, obtained by the action of phosphorus pentachloride on methylheptenone, $CMe\colon CH\cdot CH_2\cdot CH_2Ac$, loses hydrogen chloride when heated on the water-bath, yielding ζ-chloro-β-methylhepta-βε-diene, $CMe_2\colon CH\cdot CH_2\cdot CH\colon CMeCl$. The monochloroderivative, when condensed with the sodium derivative of ethyl malonate in boiling alcohol, yields diethyl βζ-dimethyl-βε-octadiene-ηθ-dicarboxylate, $CMe_2\colon CH\cdot CH_2\cdot CH\colon CMe\cdot CH(CO_2Et)_2$.

βζ-Dimethyl-βε-octadiene-θ-carboxylic acid,

$$CMe_2\colon CH\cdot CH_2\cdot CH_2\cdot CMe\colon CH\cdot CO_2H,$$

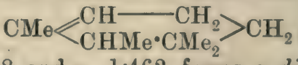
is produced on distilling the dicarboxylic acid under reduced pressure; it boils at 160° under 12 mm. pressure and is isomeric with geranic acid.

βζ-Dimethyl-βε-octadiene-θ-al, prepared by heating an intimate mixture of barium formate and the barium salt of the preceding acid, boils at 225—230°; its *semicarbazone* melts at 145° and its condensation product with cyanoacetic acid at 130°; the *oxime* and *phenylhydrazone* are oils. G. T. M.

βζ-Dimethyl-βε-octadiene-θ-al. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 119043. Compare preceding abstract).—The ethyl malonate employed in preparing βζ-dimethyl-βε-octadiene-ηθ-dicarboxylic acid may be replaced by ethyl cyanoacetate, the intermediate product, *η-cyano-βζ-dimethyl-βε-octadiene-θ-carboxylate*, being hydrolysed to the potassium dicarboxylate by 30 per cent. potassium hydroxide.

Ethyl acetoacetate, when employed in this condensation, gives rise to *ethyl βζ-dimethyl-βε-nonodiene-θ-one-η-carboxylate*, this product yielding the potassium dicarboxylate on treatment with 33 per cent. potassium hydroxide solution. G. T. M.

Reduction in the Terpene Series. Myrcene and other Olefinic Compounds. By FRIEDRICH W. SEMMLER (*Ber.*, 1901, **34**, 3122—3130).—It is shown that in the terpene series the only compounds reduced when treated with sodium and ethyl alcohol are those which contain two double linkings attached to two adjacent carbon atoms.

When reduced with sodium and alcohol, myrcene yields a *dihydromyrcene*, $C_{10}H_{18}$, which boils at 171·5—173·5°, has a sp. gr. 0·7802 and n_D 1·4501, and when treated with a mixture of acetic and sulphuric acids yields cyclo*dihydromyrcene*,  $CMe<\begin{matrix}CH\text{——}CH_2\\CHMe\cdot CMe_2\end{matrix}>CH_2$; this boils at 169—172°, has a sp. gr. 0·828 and n_D 1·462, forms a *dibromide* of sp. gr. 1·524, and when oxidised yields a ketonic *acid*, $C_{10}H_{18}O_3$. Dihydromyrcene, when oxidised with potassium permanganate, yields lævulic acid and a *ketoglycol*, $C_8H_{16}O_3$, which, when oxidised with chromic acid, forms the *diketone*, $C_7H_{12}O_2$. R. H. P.

Oil of Jasmine Blossoms. By ALBERT HESSE (*Ber.*, 1901, **34**, 2916—2932. Compare Abstr., 1900, i, 454; this vol., i, 220 and 601).—The small yield of oil obtained when jasmine flowers are subjected to steam distillation is due to the fact that the greater part of the volatile oil remains dissolved in the distillate, and may be recovered by extraction with ether, the yield being about 0·0194 per cent. The oil has a sp. gr. 0·968 at 15°, a rotation of +4°15′ in a 100 mm. tube, and a saponification number 148. It contains benzyl acetate, free benzyl alcohol, methyl anthranilate, and little or no indole, and resembles the oil obtained by extraction, except for the presence of methyl anthranilate.

The main differences between the oils obtained by the methods of extraction, steam distillation, and 'enfleurage' are that the extracted oil is free from both indole and methyl anthranilate, the distilled oil contains practically no indole, but 1·5 per cent. of anthranilate, and the oil from 'enfleurage' 2·5 per cent. of indole, and only 0·24—0·3 per cent. of methyl anthranilate.

The oil has been extracted from the blossoms which had already undergone 'enfleurage,' and it is found that the amount present is practically identical with that in the fresh blossoms; the process of 'enfleurage' thus produces some nine times the amount of oil originally present. The oil obtained from the blossoms after 'enfleurage' contains 1·5 per cent. of methyl anthranilate, but no indole. It would thus appear that methyl anthranilate does not exist as such in the fresh blossoms, but is produced during 'enfleurage' and steam distillation.

The name *ethereal jasmine oil* is suggested for the oil obtained by extraction with volatile solvents or by steam distillation, the name in the latter case to include the greater part of the oil which remains dissolved in the water, and the expression *ethereal oil of jasmine blossoms* is to be retained for the 'enfleurage' oil. J. J. S.

Essential Oil of Orange Blossoms. I. By ALBERT HESSE and OTTO ZEITSCHEL (*J. pr. Chem.*, 1901, [ii], **64**, 245—260. Compare this vol., i, 220, and preceding abstract).—A larger yield of oil is obtained by distillation than by maceration, extraction, or enfleurage. The esters present in the oil, namely, linalyl acetate and methyl anthranilate, remain nearly unchanged in the distillation.

Pure linalyl acetate, prepared from sodium linaloolate and acetic anhydride and fractionated under reduced pressure, boils at 96·5—97° under 10 mm., 115—116° under 25 mm., and at 220° (with decomposition) under atmospheric pressure, has a sp. gr. 0·913 at 15°, $[\alpha]_D$ $-6°35'$, and a saponification number 278·9.

A detailed examination of the oil is being made. K. J. P. O.

A New Aldehyde from Oil of Lemons. By HUGO VON SODEN and WILHELM ROJAHN (*Ber.*, 1901, **34**, 2809—2811).—When lemon oil, freed from citral by Tiemann's method (Abstr., 1899, i, 247), and from non-volatile constituents by distillation, is shaken with acid sodium hydrogen sulphite solution, a mixture of nonaldehyde with some octaldehyde is obtained in the form of the bisulphite compound. The authors are of opinion that the aldehyde isolated by Burgess (Proc., 1901, **17**, 171) is nonaldehyde, and point out that the fluorescent substance (m. p. 145°) obtained by him was first described by Crismer (Abstr., 1892, 349), and subsequently by Theulier (this vol., i, 218).

R. H. P.

Oil of Neroli. By HEINRICH WALBAUM (*Ber.*, 1901, **34**, 2603).—An explanation, in reply to E. and H. Erdmann (this vol., i, 601).

C. F. B.

Occurrence of Phenylethyl Alcohol in Oil of Roses. By HUGO VON SODEN and WILHELM ROJAHN (*Ber.*, 1901, **34**, 2803—2809. Compare Abstr., 1900, i, 489, and this vol., i, 39).—It is shown that oil of roses contains up to 60 per cent. of phenylethyl alcohol. The method of separating this alcohol from crude oil of roses is described.

The aqueous distillate obtained in the distillation of ylang-ylang oil contains benzyl alcohol, which is a normal, although unimportant, constituent of the oil. R. H. P.

Essence of Thyme. By PAUL JEANCARD and C. SATIE (*Bull. Soc. Chim.*, 1901, [iii], **25**, 893—895).—It is generally considered that essence of thyme should contain 25—30 per cent. of phenols, but a number of pure specimens were found to contain from 5—60 per cent. This variation depends on the manner in which the distillation is conducted, as is shown by an examination of essence of red Algerian thyme and essence of ajowan. The greater portion of the phenols passes over in the later stages of the distillation. The sp. gr. of the different fractions increases by 0·0013—0·0015 for each 1 per cent. of phenols. The surface tension, viscosity, and solubility in alcohol also increase with the proportion of phenols. N. L.

Behaviour of Caoutchouc towards Nitrous Acid. By CARL D. HARRIES (*Ber.*, 1901, **34**, 2991—2992).—Caoutchouc, when dissolved or suspended in light petroleum and subjected to the action of a rapid current of nitrous fumes evolved from arsenious oxide and nitric acid, yields a colloidal mass which gradually changes into a golden-yellow, flaky *compound*. This substance readily dissolves in ethyl acetate and is reprecipitated in a granular form on adding ether; its sinters at 95—100° and decomposes at 135°. Analyses and molecular weight determinations by the boiling point method indicate the empirical formula $C_{40}H_{62}O_{24}N_{10}$; the substance is acidic, being dissolved by dilute alkaline solutions and reprecipitated by acids.

G. T. M.

Rhododendrol, Rhododendrin, and Andromedotoxin. By Konstantin Archangelski (*Chem. Centr.*, 1901, ii, 594—595; from *Arch. exp. Path. Pharm.*, **46**, 313—320).—The leaves of *Rhododendron chrysanthum* contain the glucoside ericolin (Thal, *Pharm. Zeit. Russ.*, 1883, 209), andromedotoxin (Eykman, Abstr., 1883, 349; Plugge, Abstr., 1889, 644), and rhododendrin, together with rhododendrol, a decomposition product of rhododendrin resembling camphor. *Rhododendrol*, $C_{10}H_{12}O_2$, crystallises from water in long, colourless needles or small plates, melts at 79·5—80°, sublimes without decomposition, and is easily soluble in hot but only slightly so in cold water. When heated with nitric acid, it gives a red coloration, which becomes yellow on the addition of alkali. Its physiological effect on frogs is similar to that of camphor but on warm blooded animals it has not a poisonous effect, being excreted in the urine probably in combination with glycuronic acid. *Rhododendrin*, $C_{16}H_{22}O_7$, crystallises from water, melts at 187—187·5°, has a bitter taste, and is easily soluble in hot water or alcohol, slightly so in cold water, and only very sparingly so in chloroform or ether. It is decomposed by boiling with dilute acids forming rhododendrol and a sugar which yields an osazone melting at 194—195°. Rhododendrin has no pharmacological action. The physiological action of andromedotoxin on frogs and mammals resembles that of digitalin in its effect on the heart.

E. W. W.

Yellow Colouring Matters accompanying Chlorophyll and their Spectroscopic Relations. By C. A. Schunck (*Proc. Roy. Soc.*, 1901, **68**, 474—480. Compare Abstr., 1900, ii, 36).—The alcoholic extract of healthy green leaves, after removal of the chlorophyll, was submitted to a process of fractional extraction with carbon disulphide, and the several extracts thus obtained were submitted to spectroscopic examination. From the results obtained the author concludes that the four-banded spectrum of the crude solutions of the xanthophylls is due to a mixture of colouring matters, the chief of which is chrysophyll, which is identical with Sorby's orange xanthophyll (*Proc. Roy. Soc.*, 1873, **21**, 457), and is not due, as he formerly supposed, to a single substance which he termed xanthophyll (Abstr., 1900, ii, 36). If a small quantity of hydrochloric acid is added to a solution of chrysophyll, the effect on the spectrum is to cause the bands to fade and the solution to become gradually colourless.

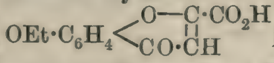
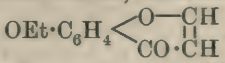
H. R. Le S.

Phthalic Acid Colouring Matters of the Naphthalene Series. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 118077).—*m*-Diethylaminohydroxybenzoylbenzoic acid and its di- and tetrachloro-derivatives yield a series of colouring matters when condensed with the sulphonic acids of the naphthols and dihydroxynaphthalenes in the presence of 50—80 per cent. sulphuric acid at 140°. These condensation products are amorphous, and their properties are exhibited in tabular form. G. T. M.

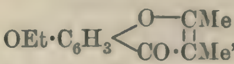
Pyromucic Anhydride. By Erich Baum (*Ber.*, 1901, **34**, 2505—2506).—Pyromucic chloride is converted by pyridine in aqueous ethereal solution into the *anhydride*, $C_{10}H_6O_5$, according to Wedekind's reaction (this vol., i, 499); it crystallises from alcohol in slender, white needles, melts at 73°, boils with slight decomposition at 325°, and with phenylhydrazine yields the phenylhydrazide of the acid.

W. A. D.

7-Hydroxychromone. By Stanislaus von Kostanecki, L. Paul, and Josef Tambor (*Ber.*, 1901, **34**, 2475—2479. Compare this vol., i, 558).—*Ethyl* 2 : 4-*diethoxybenzoyl pyruvate*, obtained by condensing resacetophenone diethyl ether with ethyl oxalate by means of sodium, crystallises from alcohol in yellowish needles and melts at 152°. *Ethyl* 2 : 5-*diethoxybenzoyl pyruvate*, obtained similarly from quinacetophenone diethyl ether, forms yellow prisms and melts at 90°; *ethyl* 2 : 4 : 6-*trimethoxybenzoyl pyruvate*, obtained from phloracetophenone trimethyl ether, crystallises in yellowish needles and melts at 80°.

Ethyl 2-*hydroxy*-4-*ethoxybenzoyl pyruvate*, obtained by the condensation of resacetophenone monoethyl ether and ethyl oxalate, crystallises from alcohol in well-formed, white needles, melts at 99—100°, and on hydrolysis with alcoholic hydrochloric acid yields 7-*ethoxychromone*-2-*carboxylic acid*,  $\mathrm{OEt{\cdot}C_6H_4}{<}\begin{matrix}\mathrm{O{-}C{\cdot}CO_2H}\\ \mathrm{CO{\cdot}CH}\end{matrix}$; this crystallises from alcohol in rosettes of prismatic needles, melts at 234°, and is thus converted into 7-*ethoxychromone*,  $\mathrm{OEt{\cdot}C_6H_4}{<}\begin{matrix}\mathrm{O{-}CH}\\ \mathrm{CO{\cdot}CH}\end{matrix}$, which separates from dilute alcohol in long needles melting at 120—121°. 7-*Hydroxychromone*, obtained by elimination of the ethyl group by hydriodic acid, crystallises from water in white sheaves of needles and melts at 218°. W. A. D.

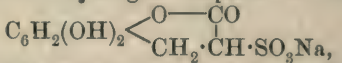
Studies in the Chromone Series. By Stanislaus von Kostanecki and Lorenzo Lloyd (*Ber.*, 1901, **34**, 2942—2950. Compare this vol., i, 222).—*Propionylresorcinol monoethyl ether*, $\mathrm{OH{\cdot}C_6H_3(COEt){\cdot}OEt}$, [OH : OEt : COEt = 1 : 3 : 6], obtained when propionylresorcinol (Abstr., 1891, 447) is alkylated by Kostanecki and Tambor's method (Abstr., 1896, i, 44), crystallises from alcohol in colourless needles melting at 54°; the *diethyl* ether, $\mathrm{COEt{\cdot}C_6H_3(OEt)_2}$, forms colourless plates melting at 72°.

7-*Ethoxy*-2 : 3-*dimethylchromone*,  $\mathrm{OEt{\cdot}C_6H_3}{<}\begin{matrix}\mathrm{O{-}CMe}\\ \mathrm{CO{\cdot}CMe}\end{matrix}$, is formed when the monoethyl ether is gently boiled for 3 hours with acetic anhydride and dry sodium acetate; it crystallises from alcohol in thick prisms melting at 124°, and gives a blue fluorescence with concentrated sulphuric acid. On hydrolysis with concentrated hydriodic acid, it yields

7-hydroxy-2 : 3-*dimethylchromone*, which crystallises in rhombic prisms melting at 262°. Its *acetyl* derivative forms long needles melting at 116°, and its ethyl ether, 7-*methoxy*-2 : 3-*dimethylchromone*, is identical with Nagai's dehydromethylacetylpaeonol (Abstr., 1892, 845). The same compound is readily obtained when propionylresorcinol is methylated according to Tahara's method, and the monomethyl ether thus obtained is boiled with acetic anhydride and dry sodium acetate.

2 : 4-*Diethoxybenzoylmethylacetone*, $C_6H_3(OEt)_2\cdot CO\cdot CHMeAc$, obtained by the action of sodium and ethyl acetate on propionylresorcinyldiethyl ether, or by the methylation of 2 : 4-diethoxybenzoylacetone (Bloch and Kostanecki, Abstr., 1900, i, 308), forms colourless plates melting at 72·5°, and when heated with hydriodic acid yields 7-ethoxy-2 : 3-dimethylchromone.

Nagai's hydroxyacetylpaeonol is undoubtedly 4-methoxybenzoylacetone. J. J. S.

Colouring Matters of the Æsculetin Series. By CARL LIEBERMANN and FRITZ WIEDERMANN (*Ber.*, 1901, **34**, 2608—2617).—Æsculetin unites with sodium hydrogen sulphite to form *sodium dihydroæsculetinsulphonate*,  $C_6H_2(OH)_2<\begin{matrix}O\text{——}CO\\ CH_2\cdot CH\cdot SO_3Na,\end{matrix}$ which is not decomposed by dilute acids and is converted by acetic anhydride into diacetylæsculetin. *Dihydroæsculetinsulphonic acid* is a hygroscopic, crystalline mass, which decomposes, when heated, into water, sulphur dioxide, and æsculetin. The sodium salt is formed from æsculetin by the combination of the sodium hydrogen sulphite with the two doubly-linked carbon atoms. Sodium dihydroæsculetinsulphonate is converted by gaseous ammonia into a deep violet-coloured compound, which was described by Rochleder (*Weiner akad. Ber.*, 1864, **48**, ii, 236 ; 1867, **55**, ii, 829) as æscorcein, $C_9H_7O_5N$, but is in reality *sodium æscorceinsulphonate*, $C_{18}H_{12}O_{16}N_2S_2Na_6$. The aqueous solution is coloured blue, and shows a blood-red fluorescence. A similar compound, which, however, contains less sodium, $C_{18}H_{13}O_{16}N_2S_2Na_5$, may be obtained by the action of ammonia on the sulphonic acid, followed by treatment of the product with sodium ethoxide in alcoholic solution.

It is converted by bromine into a *dibromo*-derivative, the sodium salt of which has the formula $C_{18}H_{11}O_{16}Br_2N_2S_2Na_5$.

Hydroæsculetin, $C_{18}H_{14}O_8$, obtained by the reduction of æsculetin with sodium amalgam, appears to be identical with the æscorcin of Rochleder, and is converted by gaseous ammonia into *dehydroæscorcein*, $C_{18}H_{13}O_7N_3$, which is a deep violet-coloured mass, and forms a blue solution in alkalis. Æsculetin itself and its direct derivatives do not yield coloured substances with ammonia, whilst the reduction products of these substances behave in a similar manner to hydroæsculetin. A. H.

Cactus Alkaloids. IV. By ARTHUR HEFFTER (*Ber.*, 1901, **34**, 3004—3015. Compare Abstr., 1895, i, 120 ; 1896, i, 267 ; 1898, i, 499).—Anhalamine, isolated by Kauder (Abstr., 1899, i, 650) from the mezcal buttons of *Anhalonium Lewinii*, yields a *hydrochloride*,

$C_{11}H_5O_3N,HCl$, crystallising slowly from water in lustrous leaflets with $2H_2O$, and from alcohol in needles with $1H_2O$; the *sulphate*, $(C_{11}H_{15}O_3N)_2,H_2SO_4$, forms colourless prisms very soluble in water, but dissolving less readily in alcohol. The *platinichloride*, $(C_{11}H_{15}O_3N)_2,H_2PtCl_6$, and the *aurichloride* crystallise respectively in yellow needles and nodules, the latter salt readily decomposing and becoming dark red. Anhalamine is optically inactive, and contains two methoxyl groups. The third oxygen atom is probably present as hydroxyl, for the alkaloid dissolves in potassium hydroxide solution, and yields a *dibenzoyl* derivative, $C_{11}H_{13}O_3NBz_2$, crystallising from alcohol or chloroform in prisms melting at 128—129°, and a *monobenzoyl* derivative, $C_{11}H_{14}O_3NBz$, melting at 167·5°. The latter product dissolves in sodium hydroxide solution and develops a blue coloration with ferric chloride. The dibenzoyl compound is insoluble in aqueous alkali hydroxides, and does not react with ferric chloride. These results indicate that anhalamine is a secondary base, having the formula $OH\cdot C_9H_7(OMe)_2{:}NH$.

Mezcaline, on oxidation with potassium permanganate first at the ordinary temperature and then at 100°, yields 2 : 3 : 4′-trimethoxybenzoic acid and a small amount of a neutral substance containing nitrogen and melting at 177°. The alkaloid is a secondary base, for its methiodide when shaken with chloroform yields *methylmezcaline*, a crystalline base, which in turn gives rise to a *methiodide*, $C_{12}H_{19}O_3N,MeI$, crystallising in pale yellow plates and melting at 220°; the corresponding *platinichloride* forms needles. *Benzoylmezcaline*, $C_{11}H_{16}O_3NBz$, readily produced by the Schotten-Baumann method, crystallises in lustrous needles and melts at 120·5°. These results indicate that mezcaline has the constitution

$$C_6H_2(OMe)_3\cdot CH_2\cdot NHMe\ [CH_2\cdot NHMe : (OMe)_3 = 1 : 3 : 4 : 5],$$

and hence it may be termed 3 : 4 : 5-*trimethoxybenzylmethylamine*.

Mezcaline or its hydrobromide readily yields *dibromomezcaline* when suspended in water and treated with bromine. The *hydrobromide* of the dibromo-base crystallises in felted needles and melts at 95°; the *hydrochloride* separates in lustrous prisms and the *sulphate*, $(C_{11}H_{15}O_3NBr_2)_2,H_2SO_4,2\frac{1}{2}H_2O$, in white needles. The *platinichloride*, crystallises in hexagonal plates melting at 230° and the *aurichloride* in orange coloured needles decomposing at 191°. The dibromo-base is only slowly oxidised by potassium permanganate even in boiling solutions, and yields dibromo-2 : 3 : 4-trimethoxybenzoic acid.

Anhalonidine, when treated with excess of benzoic chloride by the Schotten-Baumann process, yields *benzoylanhalonidine benzoate*, $C_{12}H_{13}O_3NBz_2$, a compound insoluble in sodium hydroxide solution, crystallising in prisms, and melting at 125—126°. *Benzoylanhalonidine* is precipitated by ammonium chloride from the alkaline mother liquor obtained in the benzoylation; it crystallises in lustrous plates and melts at 189°; its alcoholic solution develops a blue coloration with ferric chloride. These results point to the presence of one hydroxyl group, and one imino-radicle in the molecule of anhalonidine. This assumption is confirmed by the behaviour of the base towards methyl iodide; *methylanhalonidine hydriodide* results from the interaction of these substances in boiling methyl alcohol; it crystallises in yellow prisms and melts at 125—130°. Methylanhalonidine is an uncrystallisable base yielding crystalline salts; the *hydrochloride* forms needles and the *methiodide*, $C_{13}H_{17}O_3N,MeI,H_2O$, colourless plates or prisms sparingly soluble in cold water and melting at 199°. The iodide rendered alkaline with ammonia behaves like a solution of a quaternary base producing paralysis of the peripheral motor-nerve endings. The corresponding *platinichloride*, $(C_{14}H_{20}O_3N)_2PtCl_6$, crystallises from water in golden-yellow leaflets.

Although the constitution of anhalonidine is not yet completely determined, the foregoing results show that it may be provisionally represented by the formula $OH\cdot C_{10}H_7(OMe)_2{:}NH$. G. T. M.

Occurrence of Alkaloids and Saponins in Cactaceæ. By GEORG HEYL (*Arch. Pharm.*, 1901, **239**, 451—473).—*Pilocereus Sargentianus* contains 92 per cent. of water; from the dry drug, 7·0 per cent. of crude (5·8 of pure) alkaloid was obtained. This alkaloid, *pilocereine*, $C_{30}H_{44}O_4N_2$, is amorphous and melts at 82—86°; its *platinichloride*, with H_2PtCl_6, and *aurichloride*, with $2HAuCl_4$, were analysed. When heated with hydriodic acid by Zeisel's method, silver iodide is precipitated equivalent to 13·48 per cent. of methoxyl; some ethoxyl is undoubtedly present, however, for when the alkaloid is distilled with aqueous potassium hydroxide, the distillate gives the iodoform reaction. This alkaloid is a poison, causing cessation of the heart's action; the lethal dose for rabbits is 0·1 gram per kilogram of body-weight.

Cereus pecten aboriginum contains an alkaloid, *pectenine*, which resembles the alkaloids of *Anhalonium* in its colour reactions and physiological action. It is soluble in water and was only obtained as a syrup; a crystalline hydrochloride was prepared, however, in amount equal to 0·65 per cent. of the drug. The *platinichloride* contains Pt 23·02 per cent. The alkaloid is a poison, acting on the central nervous system and producing death by tetanic convulsions; 0·075 gram per kilogram killed a rabbit in 5 minutes.

Cereus gummosus contains no alkaloid, but a saponin, *cereic acid*, to the extent of 24 per cent. of the dry drug; the plant contains 74 per cent. of water. Cereic acid is an amorphous substance, soluble in water with an acid reaction; the solution lathers readily, especially when a little alkali is added. It contains C 58·42 and H 8·35 per cent., but no nitrogen. When it is boiled with a dilute mineral acid, insoluble *cereus-sapogenin* is precipitated and the solution acquires the power of reducing Fehling's solution. When added to a mixture of a little blood with dilute salt solution, cereic acid causes the blood corpuscles to dissolve, and is about as effective in this respect as *Quillaya*-sapotoxin. Unlike this substance, however, it is only slightly poisonous; to kill a rabbit, a dose of more than 0·1 gram per kilogram is necessary.

C. F. B.

Preparation of Mixed Carbonates of the Cinchona Alkaloids and the Mono- and Di-hydric Phenols. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 117095. Compare D.R.-P. 91370). —*Quinine phenyl carbonate*, $C_{20}H_{23}O_2N_2\cdot CO_2Ph$, prepared by heating quinine and phenyl carbonate at 120—130°, crystallises from ether or light petroleum and melts at 129°. The o-*nitrophenyl* ester,

$$C_{20}H_{23}O_2N_2\cdot CO_2\cdot C_6H_4\cdot NO_2,$$

melts at 187°. *Quinine* p-*acetylaminophenyl carbonate*,

$$C_{20}H_{23}O_2N_2\cdot CO_2\cdot C_6H_4\cdot NHAc,$$

produced by the action of *p*-acetylaminophenol on quinine dissolved in hot xylene, melts at 184°. The *thymol* derivative,

$$C_{20}H_{23}O_2N_2\cdot CO_2\cdot C_6H_3MePr^{\beta},$$

crystallises in leaflets melting at 172°; the *catechol* compound melts at 184—185°. *Cinchonidine phenyl carbonate*, $C_{19}H_{21}ON_2\cdot CO_2Ph$, melts at 89°. These compounds are obtained as colourless, tasteless, crystalline products, sparingly soluble in water or ether, but dissolving more readily in the other organic solvents; they have a basic character and combine the therapeutic action of the alkaloids and the phenols.

G. T. M.

Preparation of Quinine and Cinchonidine Alkyl Carbonates. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 118352. Compare preceding abstract and D.R.-P. 91370).—The alkyl carbonates of quinine and cinchonidine are readily obtained by treating the anhydrous salts of these alkaloids with the alkyl chlorocarbonate in an indifferent solvent such as benzene.

Quinine benzyl carbonate, produced by the action of benzyl chlorocarbonate on quinine salts, crystallises in white needles and melts at 110°; it is readily soluble in the ordinary organic solvents. G. T. M.

Quinine and Cinchonidine Chlorocarbonates. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 118122. Compare D.R.-P. 90868 and 93698 and preceding abstract).—*Quinine chlorocarbonate* is readily obtained by the action of carbonyl chloride (1 mol.) on dry quinine hydrochloride or sulphate suspended in cold chloroform; the corresponding *cinchonidine* salt is prepared in a similar manner.

G. T. M.

Oxidation of Conhydrine. By RICHARD WILLSTÄTTER (*Ber.*, 1901, 43, 3166—3171).—On oxidation with chromic acid, conhydrine yields *l*-pipecolinic acid (*l*-piperidine-2-carboxylic acid) which melts and decomposes indefinitely at about 264—265° and has $[\alpha]_D$ $-24\cdot7°$ at 24°; Mende's synthetical *l*-acid (Abstr., 1897, i, 203) melts at 270° and has $[\alpha]_D$ $-35\cdot7°$ at 20°, so that during the oxidation of conhydrine partial racemisation of the acid probably occurs. The *hydrochloride* of the *l*-acid crystallises from alcohol in sheaves of needles and melts and decomposes at 256—258°; the *copper* salt, with $3H_2O$, crystallises in deep blue rhombs and is transformed by alcohol into a *salt* with 1 mol. C_2H_6O, which forms slender, bright blue, silky needles.

The above facts show that the hydroxyl group of conhydrine is in the side-chain; the alkaloid is probably the active form of 2-β-hydroxypropylpiperidine, $C_5NH_{10}\cdot CH_2\cdot CHMe\cdot OH$, since both conhydrine and the inactive base boil at the same temperature (224—226°).

W. A. D.

Reduction of Granatonineoxime and of Methylgranatonine. By ANTONIO PICCININI and G. CORTESE (*Gazzetta*, 1901, **31**, i, 561—570).—*Granatonineoxime*, $C_8H_{14}ON_2$, prepared by a method similar to that given by Piccinini and Quartaroli (Abstr., 1899, i, 965) for the oxime of methylgranatonine, separates from a mixture of alcohol and ether in shining, colourless needles, softening at 180° and melting at 199°. Its *benzoyl* derivative, $C_{22}H_{22}O_3N_2$, crystallises from alcohol in lustrous prisms melting at 165°. The *picrate*, $C_{14}H_{17}O_8N_5$, is precipitated in needles which dissolve readily in alcohol or ether, decompose slightly at 215°, and melt at 230°.

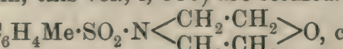
When reduced with sodium and amyl alcohol, granatonineoxime yields *ψ-granatylamine*, $C_8H_{16}N_2$, which crystallises from dry, light petroleum in small, colourless, hygroscopic prisms melting at 125°; it rapidly absorbs carbon dioxide from the air. With phenylthiocarbimide, it yields *ψ-granatylphenylthiocarbimide*, $C_{22}H_{26}N_4S_2$, which separates from methyl alcohol as a colourless, amorphous powder melting at 216°. The *picrate* of the amine, $C_{20}H_{22}O_{14}N_8$, crystallises from alcohol in small, yellow prisms which decompose without melting at between 230° and 247°. The *platinichloride*, forming pale orange-yellow prisms melting at 256° and the *aurichloride*, yellow prisms melting and slightly decomposing at 208°, were also prepared. When the oxime is reduced by means of sodium amalgam and acetic acid, ψ-granatylamine is formed, together with an isomeric amine; the latter could not be separated, but its *aurichloride*, $C_8H_{16}N_2,H_2Au_2Cl_8$, is deposited in the form of long, golden-yellow, thread-like crystals melting at 238—239°.

When reduced with either zinc and acetic acid, tin and hydrochloric acid, or sodium and amyl alcohol, methylgranatonine is completely converted into methylgranatoline. The latter is also formed, but not as sole product, when the reduction is effected with sodium amalgam and water, *methylgranatonine pinacone*, $C_{18}H_{32}O_2N_2$, being also formed in this case. This compound crystallises from alcohol in colourless, acicular prisms melting at 248°; it is slightly soluble in water, benzene, or ether, and forms salts with acids. Its *aurichloride*, $C_{18}H_{32}O_2N_2,H_2Au_2Cl_8$, separates from water in yellow prisms melting at 229°, whilst the *platinichloride* is deposited from dilute hydrochloric acid in prisms which decompose at about 260°, leaving a residue melting at 285°. The *picrate*, $C_{30}H_{38}O_{16}N_8$, separates from dilute alcohol in crystals which decompose without melting at 260°. The pinacone precipitates silver oxide from silver nitrate solution. With mercuric chloride, the hydrochloride of the pinacone yields a *mercurichloride* separating in aggregates of thin needles which soften at 240° and melt at 247°. T. H. P.

Alkaloids of Mandragora Roots. By OSWALD HESSE (*J. pr. Chem.*, 1901, [ii], **64**, 274—286. Compare Thoms and Wentzel, this vol., i, 405).—The author has investigated the alkaloids accompanying hyoscyamine in mandragora roots, using the method of extraction which Wentzel employed. The solution of the alkaloids in sulphuric acid is neutralised with sodium hydrogen carbonate and then extracted with chloroform. The alkaloid thus obtained is shown to be a hyoscine of the formula $C_{17}H_{21}O_4N$, and not of the formula $C_{17}H_{23}O_3N$, as found by Wentzel. On hydrolysis, the hyoscine yields tropic acid and oscine, $C_8H_{13}O_2N$.

The hyoscine was accompanied by a small quantity of ψ-hyoscyamine, and of a new alkaloid, *mandragorine.* This base was separated from the mother liquor, from which the ψ-hyoscyamine had been extracted, by addition of sodium carbonate and chloroform; the *aurichloride*, $C_{15}H_{19}NO_2,HAuCl_4$, forms a crystalline powder melting at 124—126°; hydrolysis with barium hydroxide yields atropic acid and a base resembling tropine. K. J. P. O.

Preparation of Morpholine from Ethylene by means of the Mercury Ethyl Ether Salt. By Julius Sand (*Ber.*, 1901, **34**, 2906—2910).—The constitution previously ascribed to the di-iodoethyl ether (*Ber.*, 1901, **34**, 1391), namely, $O(CH_2{\cdot}CH_2I)_2$, is confirmed by the fact that when the ether is condensed with *p*-toluenesulphonamide (Marckwald, Abstr., 1899, i, 289), and then hydrolysed with 25 per cent. hydrochloric acid at 170°, *p*-toluenesulphonic acid and morpholine hydrochloride (Marckwald and Chain, this vol., i, 380) are formed.

p-*Toluenesulphomorpholinamide*,  $C_6H_4Me{\cdot}SO_2{\cdot}N{<}^{CH_2{\cdot}CH_2}_{CH_2{\cdot}CH_2}{>}O$, crystallises from alcohol in long, glistening prisms melting at 147°.

Ammonia itself does not convert the di-iodoethyl ether into morpholine, but yields a *tertiary* base, the *picrate* of which melts at 123°. J. J. S.

Morpholine. Wilhelm Marckwald & Michael Chain (D.R.-P. 119785).—*Nitrosophenylmorpholine*, obtained by treating a concentrated hydrochloric acid solution of phenylmorpholine with sodium nitrite and decomposing the precipitated *hydrochloride* with sodium carbonate, crystallises from water in lustrous leaflets melting at 100°.

Dinitrophenylmorpholine results from the action of 33 per cent. nitric acid on phenylmorpholine; it crystallises from alcohol in orange-yellow needles melting at 118°.

These compounds, when boiled with 10 per cent. sodium hydroxide solution, yield morpholine together with *p*-nitrosophenol and 2 : 4-dinitrophenol respectively. G. T. M.

Morpholine and its Derivatives. Wilhelm Marckwald & Michael Chain (D.R.-P. 120047).—Sulphonamides, when treated with bromoethyl aryl ethers, $CH_2Br{\cdot}CH_2{\cdot}O{\cdot}Ar$ (2 mols.), and sodium hydroxide (2 mols.), yield diaryl ethers of the corresponding sulphondiethanolamides, $R{\cdot}SO_2{\cdot}N(CH_2{\cdot}CH_2{\cdot}OAr)_2$, and these compounds, when hydrolysed with 25 per cent. hydrochloric acid at 170°, yield morpholine or one of its derivatives. For example, *p*-toluenesulphonamide, when treated with bromoethyl β-naphthyl ether,

$$CH_2Br{\cdot}CH_2{\cdot}O{\cdot}C_{10}H_7,$$

gives rise to the di-β-naphthyl ether of *p*-toluenesulphondiethanolamide, $C_7H_7{\cdot}SO_2{\cdot}N(CH_2{\cdot}CH_2{\cdot}O{\cdot}C_{10}H_7)_2$, and this product (m. p. 130°), when hydrolysed, yields morpholine, β-naphthol, toluene, and sulphuric acid. Morpholine is also obtained from *p*-toluenesulphonaminoethyl phenyl ether, $C_7H_7{\cdot}SO_2{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}OPh$ (m. p. 104°), by condensing this with ethylene chlorohydrin and hydrolysing the product, $OH\cdot CH_2\cdot CH_2\cdot N(SO_2\cdot C_7H_7)\cdot CH_2\cdot CH_2\cdot OPh$ (m. p. 73°), with 25 per cent. hydrochloric acid.

Methylmorpholine may be prepared from methyliminoethyl phenyl ether, $NMe(CH_2\cdot CH_2\cdot OPh)_2$, this compound being obtained, together with methylaminoethyl phenyl ether, $NHMe(CH_2\cdot CH_2\cdot OPh)$, by the action of bromoethyl phenyl ether on a dilute alcoholic solution of methylamine. The secondary base is removed as a nitrosoamine, whilst the tertiary base is hydrolysed at 160°, yielding methylmorpholine hydrochloride. G. T. M.

Preparation of Morphenol. By EDUARD VONGERICHTEN (*Ber.*, 1901, **34**, 2722—2723).—The conversion of β-methylmorphimethine methiodide into morphenol (Abstr., 1900, i, 248) is best effected by heating with alcoholic potassium hydroxide in sealed tubes at 160°. Similar treatment of the dihydro-compound (Abstr., 1899, i, 551) gives trimethylamine and a compound free from nitrogen, whereas morphine and codeine have been shown to give methylethylamine, and codeine methiodide gives dimethylethylamine (Skraup and Wiegmann, Abstr., 1889, 1018; 1890, 179). T. M. L.

Alkaloids of the Papaveraceæ. By ERNST SCHMIDT (*Arch. Pharm.*, 1901, **239**, 395—408).—An introduction to the following four papers (compare also Henschke, Abstr., 1889, 62; Selle, Abstr., 1890, 649; 1891, 229; Koenig and Tietz, Abstr., 1893, i, 490). The presence of sanguinarine in the root of *Chelidonium majus* was ascertained with certainty by isolating this alkaloid from the residues obtained in the preparation of chelidonine on the large scale.

Protopine has now been prepared by pupils of the author from *Chelidonium majus*, *Stylophoron diphyllum*, *Sanguinaria canadensis*, *Eschscholtzia californica*, and *Glaucium luteum*, and shown in all cases to have the formula $C_{20}H_{19}O_5N$. The same alkaloid has been isolated by others from *Papaver somniferum*, *Macleaya cordata*, and *Bocconia frutescens*, and consequently has some claim to be regarded as the typical alkaloid of the *Papaveraceæ*. Moreover, it has just been isolated from *Fumaria officinalis* by Trowbridge in the author's laboratory, and probably it is this substance which has been described under different names as occurring in various other plants allied with the *Papaveraceæ*. It forms monoclinic crystals [$a:b:c = 0·8992:1:?$; $\beta = 57°19'$.]

β- and γ-Homochelidonine appear to be physical isomerides, with the formula $C_{21}H_{23}O_5N$. α-Homochelidonine, on the other hand, appears to have a different formula, $C_{21}H_{21}O_5N$.

Glaucine, it is pointed out, may be a lower homologue of corydaline. Its physiological action (which is described) is similar to that of other *Papaveraceæ* alkaloids, but has characteristics of its own. C. F. B.

Alkaloids of Sanguinaria Canadensis. By RICHARD FISCHER (*Arch. Pharm.*, 1901, **239**, 409—420).—Chelerythrine, sanguinarine, homochelidonine, and protopine were isolated from the roots of *Sanguinaria canadensis*; the method employed is detailed in the paper. Chelerythrine turns yellow in air containing carbon dioxide. When crystallised from solvents containing alcohol it melts at 203° and has the composition $C_{21}H_{17}O_4N,EtOH$ (Schmidt, Koenig, and Tietz, Abstr., 1893, i, 490). When crystallised from toluene, however, it melts at 257° and has the composition $2C_{21}H_{17}O_4N,H_2O,C_6H_5Me$; the toluene is lost at 100°, but the water not even at 140°.

The sanguinarine obtained melted at 211° and had the composition $2C_{20}H_{15}O_4N,EtOH$.

The homochelidonine was obtained in two forms, β and γ, melting at 159° and 169° respectively; the latter crystallises from alcohol and ethyl acetate respectively with the composition $2C_{21}H_{23}O_5N +$ EtOH, or + EtOAc. These forms appear to be physical isomerides; each can be converted into the other readily by the employment of a suitable precipitant, temperature, or solvent.

The protopine melted at 206—207°, had the composition $C_{20}H_{19}O_5N$, and crystallographically also was identical with a specimen prepared from *Chelidonium majus*. C. F. B.

Alkaloids of Eschscholtzia Californica. By RICHARD FISCHER (*Arch. Pharm.*, 1901, **239**, 421—425).—All parts of the plant were worked up together, with the result that protopine and β- (or γ-) homochelidonine were isolated, identical with the substances obtained from *Sanguinaria*. Traces of chelerythrine and sanguinarine were probably obtained also. The method employed is described in detail.

C. F. B.

Alkaloids of Glaucium Luteum. By RICHARD FISCHER (*Arch. Pharm.*, 1901, **239**, 426—437).—The stem, leaves, and flowers of this plant were worked up together and found to contain protopine, identical with that from *Sanguinaria* and *Eschscholtzia*, and glaucine. In the root protopine was found, and probably traces of chelerythrine and sanguinarine. No homochelidonine was detected in either case. The method employed is described in detail.

Glaucine has been described already by Probst, but evidently his substance was still quite impure. It has the composition $C_{17}H_{13}N(OMe)_4$; it crystallises, although not readily, from ethereal solution in rhombic prisms [$a:b:c = 0·5797:1:0·2718$], melts at 119—120°, and has $[\alpha]_D$ $+113·3°$ in 5 per cent. alcoholic solution. It is not very stable in air and sunlight, undergoing oxidation readily. It is a very weak base; the *hydrochloride*, with 1HCl and $3H_2O$, and *hydrobromide*, with 1HBr, were analysed. It reacts like a tertiary base with 1 mol. of methyl iodide, forming a *methiodide* which is not decomposed by alkalis; this compound melts at 216°. When it is heated with hydriodic acid, glaucine reacts as though it contained four methoxyl groups; crystals are formed which melt at 225—235°, readily undergo oxidation, and have the composition $C_{17}H_{13}N(OH)_4,HI$. C. F. B.

Alkaloids of Chelidonium Majus. By M. WINTGEN (*Arch. Pharm.*, 1901, **239**, 438—451).—A commercial sample of chelidonine was recrystallised from chloroform-alcohol and then found to have the melting point 135—136° and the composition $OH·C_{20}H_{18}O_4N,H_2O$. The *phosphate*, with $1H_3PO_4$, and *hydriodide*, with 1HI, were analysed; the latter is colourless when pure, but soon turns yellow in air and sunlight.

The acetyl derivative melted at 161°; its *aurichloride* and *platinichloride* are amorphous and melt at 155° and 204° respectively. The benzoyl derivative melted at 210—211°. Attempts to reduce chelidonine with sodium amalgam or with sodium and boiling alcohol, or to oxidise it with barium permanganate in alkaline solution, had negative results. Bromine converts it, in the presence of water, into a *perbromide*, $C_{20}H_{18}O_5NBr,HBr,Br_2$, which is reduced in alcoholic solution by sodium amalgam, or by zinc powder and dilute sulphuric acid, or by hydrogen sulphide, to *bromochelidonine*, $C_{20}H_{18}O_5NBr$. This melts at 225—230° and forms an amorphous *platinichloride* and *aurichloride* melting at 231° and 137—138° respectively. When a solution of chelidonine in dilute sulphuric acid is allowed to remain with hydrogen peroxide, crystals of a *peroxide*, $C_{20}H_{19}O_6N,H_2O$, are formed; this substance is reduced by sulphurous acid and by nascent hydrogen, but it does not liberate iodine from a solution of potassium iodide; with gold chloride solution, it yields the aurichloride of chelidonine. In 2 per cent. solution in 96 per cent. alcohol, chelidonine has $[\alpha]_D$ 115°24′; in 1 per cent. solution, 150°59′; in 2 per cent. chloroform solution, 117°21′. The sulphate, in 2 per cent. aqueous solution, has $[\alpha]_D$ 90°56′.

Protopine, $C_{20}H_{19}O_5N$, and chelerythrine, $C_{20}H_{17}O_4N,EtOH$, were prepared from residues obtained in the commercial preparation of chelidonine, and separated by means of their different solubility in ethyl acetate. The protopine melted at 207°; its crystalline aurichloride, with $HAuCl_4$, and platinichloride, with $\frac{1}{2}H_2PtCl_6,H_2O$, were analysed.

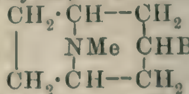
The chelerythrine melted at 203—204°; its brownish-yellow, amorphous aurichloride, with $HAuCl_4$, and yellow, crystalline platinichloride, with $\frac{1}{2}H_2PtCl_6$, and sulphate, with $H_2SO_4,2H_2O$, were analysed.

From residues of similar origin homochelidonine was obtained in two forms. One, γ, crystallised from alcohol, melted at 169—170°, effloresced readily, and formed monoclinic crystals

$$[a : b : c = 0{\cdot}9883 : 1 : 1{\cdot}4035 ;\ \beta = 76°8′].$$

The other, β, also formed monoclinic crystals, but melted at 160°, and did not effloresce. Both yield the same blood-red, crystalline aurichloride, with $HAuCl_4$, melting at 187°, and yellow, amorphous platinichloride, with $\frac{1}{2}H_2PtCl_6$, containing some water in addition.

C. F. B.

Conversion of Tropidine into Tropine. By Richard Willstätter (*Ber.*, 1901, **34**, 3163—3165).—The hydrogen bromide additive compound of tropidine is a 3-*bromotropan*,  $\begin{array}{l} CH_2\cdot CH{-}{-}CH_2 \\ \vert \qquad NMe \quad CHBr \\ CH_2\cdot CH{-}{-}CH_2 \end{array}$, for on reduction its methiodide yields exclusively tropan methiodide, and thus differs from 2-bromotropan which gives Δ^3-methyltropan (this vol., i, 223). The author failed to replace the bromine atom by hydroxyl, either directly by using silver oxide or alkalis, or, indirectly, by means of silver acetate, alkali acetates, or ammonia; in all cases, tropidine or amorphous products were formed. By heating the bromotropan, however, with 10 per cent. sulphuric acid for 3 hours at 200—210°, a mixture of tropidine and ψ-tropine was obtained; as ψ-tropine is readily transformed into tropine (Abstr., 1900, i, 404), the complete synthesis of atropine and other solanaceous alkaloids has been realised. W. A. D.

Production of Pyrrolidine-2-carboxylic Acid and of Phenylalanine by the Hydrolysis of Egg-Albumin. By Emil Fischer (*Zeit. physiol. Chem.*, 1901, **33**, 412—416).—Egg-albumin has been treated in exactly the same manner as casein (this vol., p. 780). The products of hydrolysis were esterified and fractionally distilled. Pyrrolidine-2-carboxylic acid was isolated from the fraction boiling at 90—110° under 25 mm. pressure, and phenylalanine from that boiling at 145—165° under 25 mm. pressure.

The same products may be obtained from gelatin. J. J. S.

Action of Aminosulphonic Acid on Piperidine. By Carl Paal and M. Hubaleck (*Ber.*, 1901, **34**, 2757—2763. Compare this vol., i, 693).—On heating piperidine aminosulphonate with excess of the base at 150—200°, a piperidinesulphonic acid is obtained in which the group SO_3H is attached to a carbon atom; the intermediate compound in which the sulphonic group is attached to the nitrogen atom could not be isolated.

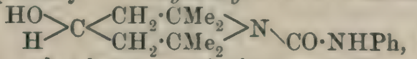
Piperidine aminosulphonate, $C_5NH_{11},NH_2\cdot SO_3H$, prepared by adding aminosulphonic acid to an alcoholic solution of piperidine, crystallises in white, hygroscopic leaflets melting at 62°.

Piperidine-C-sulphonic acid, $C_5NH_{10}\cdot SO_3H$, prepared by heating this salt with piperidine under pressure at 180°, crystallises in long, white, spear-like forms which melt at 187—188°. The *potassium* salt is a pale yellow powder; the *barium* salt, with H_2O, and the *silver* salt crystallise in leaflets. Oxidation of the sulphonic acid with silver acetate produced pyridine and sulphuric acid. On distilling the sulphonic acid with potassium hydroxide, a tetrahydropyridine is formed; it is probably the Δ^3-derivative, as it appears not to be identical with Δ^5-tetrahydropyridine, prepared by Wolffenstein (Abstr., 1892, 1484), and the acid is therefore the 3- or the 4-piperidinesulphonic acid. The *aurichloride* of the base is a crystalline powder melting and decomposing at 141—142°, and the *benzoyl* derivative a pale yellow oil.

Piperidine-1-sulphonic acid can be prepared by treating an ethereal solution of piperidine with sulphur trioxide; the *barium* salt is a crystalline powder which is decomposed immediately by hydrochloric acid into barium sulphate and piperidine. The free N-sulphonic acid cannot be isolated, as in aqueous solution it is rapidly transformed into the C-sulphonic acid just described. K. J. P. O.

Isomerism in the Piperidine Series. By Erich Groschuff (*Ber.*, 1901, **34**, 2974—2978. Compare Marcuse and Wolffenstein, this vol., i, 608).—α-Vinyldiacetonealkamine [4-hydroxy-2:2:6:6-tetramethylpiperidine] on treatment with phenylcarbimide gives rise to two isomeric products which are considered to be stereoisomeric carbamides.

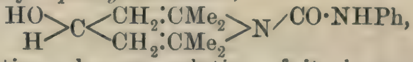
The "primary" *4-hydroxy-2:2:6:6-tetramethylpiperidylphenylcarbamide*,



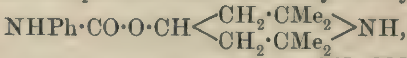
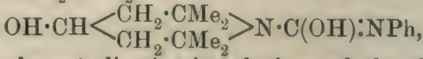
$\begin{matrix}HO\\H\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\cdot CMe_2\\CH_2\cdot CMe_2\end{matrix}\!>\!N\cdot CO\cdot NHPh$,

produced from its generators in a hot benzene solution, crystallises from this solvent in needles melting at 136°; its *hydrochloride* melts at 254° and is decomposed by water.

The "secondary" *phenylcarbamide*,



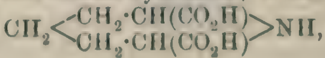
$$\begin{matrix}HO\\H\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\cdot CMe_2\\CH_2\cdot CMe_2\end{matrix}\!>\!N{\diagup}CO\cdot NHPh,$$

obtained by heating a benzene solution of its isomeride for 40 hours, melts at 147°; it is seven times as soluble in benzene as the primary compound, but dissolves to the same extent in other solvents; its *hydrochloride* melts at 237°. This isomeride, when heated with concentrated hydrochloric acid at 110°, regenerates the original base. Since these compounds are both very feebly basic, the alternative formula,  $NHPh\cdot CO\cdot O\cdot CH\!<\!\begin{matrix}CH_2\cdot CMe_2\\CH_2\cdot CMe_2\end{matrix}\!>\!NH$, is excluded; neither is the tautomeric structure,  $OH\cdot CH\!<\!\begin{matrix}CH_2\cdot CMe_2\\CH_2\cdot CMe_2\end{matrix}\!>\!N\cdot C(OH)\colon NPh$, admissible, for the isomerides do not dissolve in solutions of the alkali hydroxides.

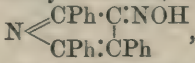
The corresponding *phenylcarbamides* of triacetonealkamine melt respectively at 129° and 138°. G. T. M.

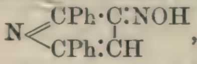
Synthesis of 2:6-Piperidinedicarboxylic Acids. By EMIL FISCHER (*Ber.*, 1901, **34**, 2543—2549).—Ethyl dibromopimelate, $CH_2(CH_2\cdot CHBr\cdot CO_2Et)_2$ (Willstätter, Abstr., 1895, i, 338), was sealed up with liquid ammonia in a pressure tube (cooled with liquid air during the operation) and allowed to remain several days at the ordinary temperature; the tube was then opened (while cooled as before) and the contents evaporated. The residue was a mixture of an amide with the hydrobromide of an isomeric amide. It was extracted with a small quantity of cold water, and the residue crystallised from a little hot water; in this way α-2:6-*piperidinedicarboxylamide* was obtained in amount equal to 17 per cent. of the original ester. It crystallises with $1H_2O$, melts at 228—229° (corr.) whether dehydrated or not, and forms a *hydrobromide*, with 1HBr, which melts and decomposes at about 290°. When boiled with excess of aqueous barium hydroxide, it is hydrolysed to α-2:6-*piperidinedicarboxylic acid*; this melts and decomposes at 258° (corr.), crystallises with $1H_2O$, and forms a blue, crystalline *copper* salt which is only slightly soluble in cold water, and so may be utilised in the isolation of the acid.

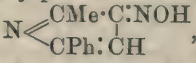
On concentration, the mother liquor of the amide just described yielded crystals in amount equal to 15 per cent. of the original ester. These were recrystallised repeatedly from small quantities of boiling water, and were then found to melt and decompose at 280° and to contain 1HBr. This *hydrobromide* was decomposed with silver oxide, when β-2:6 *piperidinedicarboxylamide* was obtained in yield equal to 73 per cent. of the theoretical; it melts at 225—226° (corr.). The corresponding β-2:6-*piperidinedicarboxylic acid* was prepared from the hydrobromide, in yield equal to 93 per cent. of the theoretical, by successive treatment with aqueous barium hydroxide, carbon dioxide, silver sulphate, hydrogen sulphide, and barium hydroxide; it melts at 281° (corr.).

These two acids,  $CH_2\!<\!\begin{matrix}CH_2\cdot CH(CO_2H)\\CH_2\cdot CH(CO_2H)\end{matrix}\!>\!NH$, and their amides are doubtless stereoisomeric, one pair being *cis*-, and the other *cis trans*-forms (compare Besthorn, Abstr., 1896, i, 252). C. F. B.

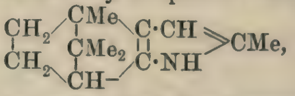
3-Nitrosopyrroles. By FRANCESCO ANGELICO and E. CALVELLO (*Gazzetta*, 1901, **31**, ii, 4—14. Compare Spica and Angelico, Abstr., 1899, i, 938, and Angeli and Angelico, this vol., i, 45).—By the action of amyl nitrite on the pyrroles in presence of sodium ethoxide, the sodium salts of the corresponding nitroso-derivatives are formed; these salts are less soluble in water than those of the nitrosoindoles (*loc. cit.*) and their solutions have a more intense yellow colour. The action of carbon dioxide on the salts yields the nitrosopyrroles which react readily with acetic anhydride, benzoyl chloride, &c.

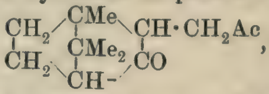
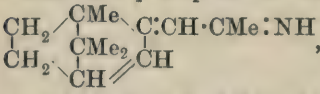
4-*Nitroso*-2 : 3 : 5-*triphenylpyrrole*,  $\mathrm{N}\!<\!\begin{matrix}\mathrm{CPh\cdot C{:}NOH}\\ \mathrm{CPh{:}CPh}\end{matrix}$, obtained by gradually adding amyl nitrite (1 mol.) to a mixture of sodium ethoxide (1 mol.) and 2 : 3 : 5-triphenylpyrrole (1 mol.), separates from benzene in sparkling, yellowish-brown scales, or from alcohol in shining golden-yellow needles melting and decomposing at 197—199°. It combines with phenylcarbimide, whilst the sodium salt reacts readily with ethyl iodide or benzoyl chloride and gives yellowish or reddish precipitates with silver nitrate, ferric, barium, or platinum chloride, copper sulphate, or uranium acetate. The *ethyl* ester, $C_{22}H_{15}N{:}NOEt$, prepared from the nitroso-compound by the action of sodium ethoxide and ethyl iodide, crystallises from light petroleum in reddish-brown needles melting at 125°. The *benzoyl* derivative, $C_{29}H_{20}O_2N_2$, crystallises from alcohol in dark red needles melting at 189°. With phenylcarbimide, the nitroso-derivative gives the *compound* $C_{22}H_{15}N{:}N\cdot O\cdot CO\cdot NHPh$, which separates from benzene in dark red needles melting at 142°.

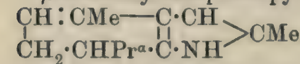
3-*Nitroso*-2 : 5-*diphenylpyrrole*,  $\mathrm{N}\!<\!\begin{matrix}\mathrm{CPh\cdot C{:}NOH}\\ \mathrm{CPh{:}CH}\end{matrix}$, prepared from 2 : 5-diphenylpyrrole and amyl nitrite in presence of sodium ethoxide, crystallises from benzene or xylene in small, shining, maroon needles melting and decomposing at 204°. With phenylcarbimide, it yields a *compound* which forms a brownish-grey powder melting at 193—194°.

3-*Nitroso*-5-*phenyl*-2-*methylpyrrole*,  $\mathrm{N}\!<\!\begin{matrix}\mathrm{CMe\cdot C{:}NOH}\\ \mathrm{CPh{:}CH}\end{matrix}$, prepared from the corresponding phenylmethylpyrrole, is obtained by the action of carbon dioxide on a solution of the sodium salt as a yellowish-brown powder which becomes intensely brown at 160° and black at 240°, at which temperature it is still unmelted; it is soluble in alkalis and combines with phenylcarbimide. T. H. P.

A Characteristic Fission of the Pyrrole Ring. By PAUL DUDEN and D. HEYNSIUS (*Ber.*, 1901, **34**, 3054—3062. Compare Abstr., 1900, i, 671—674).—*a*-2-*Methylcamphenepyrrole*-3-*carboxylic acid*, obtained on hydrolysing its ethyl ester with a dilute alcoholic solution of sodium hydroxide, crystallises from alcohol in prisms melting at 246°; its hydrochloric acid solution gives a slight pyrrole reaction, and the acid itself, when warmed with 40 per cent. sulphuric acid, changes into the isomeric β-acid. These isomerides are distinguished from each other by their different solubilities in ether, this solvent dissolving 60 parts of the β-acid but only 0·5 part of the α-compound.

α-2-*Methylcamphenepyrrole*,  , prepared by distilling the preceding compound under diminished pressure, is a very unstable crystalline substance, rapidly becoming red; it melts at 65° and is readily soluble in all the organic solvents excepting light petroleum. The *picrate* melts at 116°.

This base, which has an odour resembling that of hydrocyanic acid, is decomposed by dilute sulphuric acid, yielding a γ-diketone, *acetonyl*iso*camphor*, , an oil boiling at 290—291° and having n_D 1·485 at 22° and a sp. gr. 1·029 at 22°/4°. The *disemicarbazone*, a microcrystalline powder, melts at 215°; the *phenylhydrazone* crystallises in leaflets melting at 128—129°, and the p-*bromophenylhydrazone* in prisms melting at 154—156°. The *imide*, $C_{13}H_{21}ON$ (compare this vol., i, 163), formed from the diketone by the action of alcoholic ammonia, crystallises in needles and melts at 151°; it sublimes in woolly needles and is decomposed into its generators on boiling with alcohol or water. α-2-Methylcamphenepyrrole yields on reduction equal parts of the diketone and *methylcamphenepyrroline*, , a pale yellow oil boiling at 246—248°; the *picrate* and *platinichloride* melt at 200° and 210° respectively.

β-2-Methylcamphenepyrrole is now considered to have the formula 

$$\begin{matrix} CH\!:\!CMe\text{---}C\cdot CH \\ | \qquad\qquad\quad \| \\ CH_2\cdot CHPr^a\cdot C\cdot NH \end{matrix}\!\!>\!CMe$$

, and when prepared from sodium β-methylcamphenepyrrolecarboxylate it is accompanied by a solid isomeride, γ-2-*methylcamphenepyrrole*, the two products being separated by fractional crystallisation from light petroleum. The new compound melts at 43°, and closely resembles the β-isomeride in chemical properties; both substances give a well-marked pyrrole reaction and do not lose ammonia when treated with dilute sulphuric acid. G. T. M.

Chloro-derivatives of the Pyridine Bases. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 116386. Compare D.R.-P. 109933).—The alkyl and aryl chlorocarbonates interact with pyridine, yielding compounds of the type $OR\cdot C_5NH_5\cdot CO\cdot C_5NH_5Cl$. These substances, when treated with alcohols or phenols, decompose, giving rise to a mixture of pyridine hydrochloride, pyridine, and the corresponding mixed carbonate, $RO\cdot CO\cdot OR'$. The following *compounds*,

$$OEt\cdot C_5NH_5\cdot CO\cdot C_5NH_5Cl,$$

$$OMe\cdot C_5NH_4Me\cdot CO\cdot C_5NH_4MeCl, \text{ and}$$

$$OPh\cdot C_5NH_3Me_2\cdot CO\cdot C_5NH_3Me_2Cl,$$

are described; they are unstable, hygroscopic, yellow substances, and are rapidly decomposed by water.

G. T. M.

Resolution of an Optically Inactive Base by an Active Alkyl Haloid. By MAX SCHOLTZ (*Ber.*, 1901, **34**, 3015—3020).—The product of the action of active amyl iodide ($[\alpha]_D$ +4·50°) on 1-methyl-2-pipecoline at 100° consists of a mixture of crystalline and syrupy quaternary iodides. These substances, when heated at 200° with aqueous ammonia, lose methyl iodide and become converted into the same 1-amyl-2-pipecoline. It follows from this that the optically active iodide combines equally readily with both the optically active constituents of 1-methyl-2-pipecoline, and does not effect any resolution of this racemic base. The solid 1-*methyl*-2-*pipecoline amyliodide* crystallises in prisms, melts at 214°, and has $[\alpha]_D$ +4·4° at 20°; the corresponding *platinichloride*, $(C_{12}H_{26}N)_2PtCl_6$, and *aurichloride* crystallise in needles melting respectively at 239—240° and 140—141°. 1-amyl-2-pipecoline boils at 200—202° under 750 mm. pressure; it has a sp. gr. 0·8302 at 20° and $[\alpha]_D$ +2·77° to 3·04° at 20°; its *platinichloride* crystallises in pyramids melting at 196°; the *aurichloride* forms leaflets melting at 142°. G. T. M.

Condensations of the Ester of *iso*Nicotinic Acid. By RUDOLF TSCHERNE (*Monatsh.*, 1901, **22**, 615—626. Compare Micko, Abstr., 1897, i, 96, and Ferenczy, Abstr., 1898, i, 271).—4 *αγ-Diketobutylpyridine* [4-*aceto-acetylpyridine*], $C_5NH_4{\cdot}CO{\cdot}CH_2Ac$, is prepared by dropping an ethereal solution of ethyl *iso*nicotinate and acetone on to alcohol-free sodium ethoxide; the product of the reaction is treated with water and carbon dioxide and extracted with benzene; it crystallises in colourless needles melting at 62°, and boils at 145—147° under 18 mm. pressure. The alcoholic solution gives a dark red coloration with ferric chloride. Boiling concentrated potassium hydroxide slowly decomposes it into acetone and *iso*nicotinic acid. The *platinichloride*, forms reddish-brown, lustrous leaflets decomposing at 228°; the methiodide, golden-yellow needles. The *mono-oxime*, $C_5NH_4{\cdot}CO{\cdot}CH_2{\cdot}CMe{:}N{\cdot}OH$, forms colourless, lustrous crystals melting at 164—165°. When the alcoholic solution of 4-acetoacetylpyridine is boiled with aniline hydrochloride, an *anilide*, $C_5NH_4{\cdot}CO{\cdot}CH_2{\cdot}CMe{:}NPh$, is obtained, crystallising in yellow leaflets which melt at 103—104°; dilute alkalis and acids bring about the elimination of aniline. 2-*Methyl*-4-*pyridylquinoline*,

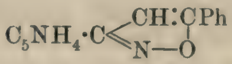
$$C_5NH_4{\cdot}C_9NH_5Me,$$

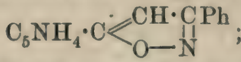
prepared when the anilide is heated with concentrated sulphuric acid, forms white crystals melting at 101—102°.

4-*αγ-Diketo-γ-phenylpropylpyridine* [4-*benzoacetylpyridine*],

$$C_5NH_4{\cdot}CO{\cdot}CH_2{\cdot}COPh,$$

prepared from ethyl *iso*nicotinate and acetophenone, crystallises in colourless needles melting at 80°, and boils at 233° under 18 mm. pressure: the alcoholic solution gives a deep red colour with ferric chloride. The *hydrochloride* crystallises in greenish-yellow needles with a silky lustre; the *platinichloride* forms a dark yellow, crystalline powder. With hydroxylamine, an oxime is not formed, but when an alcoholic solution of 4-benzoacetylpyridine is boiled with hydroxylamine hydrochloride, an iso*oxazole* derivative is formed

which has the constitution 
$C_5NH_4\cdot C\left\langle\begin{array}{l}CH{:}CPh \\ N{-}O\end{array}\right.$ or


$C_5NH_4\cdot C\left\langle\begin{array}{l}CH\cdot CPh \\ O{-}N\end{array}\right.$;

it crystallises in white leaflets, with a silvery lustre, melts at 165°, and is not decomposed by boiling with potassium hydroxide or dilute acids. K. J. P. O.

Ester-Formation with Pyridinepolycarboxylic Acids. By HANS MEYER (*Monatsh.*, 1901, **22**, 577—586. Compare this vol., i, 407).—Methyl hydrogen phthalate yields, with thionyl chloride, the chloride $COCl\cdot C_6H_4\cdot CO_2Me$, which is a colourless oil decomposing at 100° into phthalic anhydride and methyl chloride. With methyl alcohol, it gives dimethyl phthalate, and with ethyl alcohol, *methyl ethyl phthalate*; the latter is a colourless oil boiling at 285—287°. With thionyl chloride, ethyl hydrogen phthalate similarly yields an acid chloride (compare Zelinsky, Abstr., 1887, 669).

2-*Methyl quinolinate* 3-*chloride*, ($COCl\cdot C_5NH_3\cdot CO_2Me$), prepared by warming 2-methyl 3-hydrogen quinolinate with thionyl chloride, crystallises in colourless needles melting and decomposing at 126°; with methyl alcohol, it gives the *hydrochloride* of the dimethyl ester as colourless hygroscopic needles melting at 56°. 2-*Methyl* 3-*ethyl quinolinate* is formed when the methyl ester chloride is treated with ethyl alcohol; it is a colourless oil boiling and decomposing at 250—255°; the hydrochloride is hygroscopic; the *platinichloride* forms orange red crystals melting and decomposing at 165°. 2-*Ethyl quinolinate* 3-*chloride* melts at 163°, and with methyl alcohol gives 3-*methyl* 2-*ethyl quinolinate*, an oil which boils and decomposes at 254—258°; the *platinichloride* crystallises in straw-yellow needles melting at 174°.

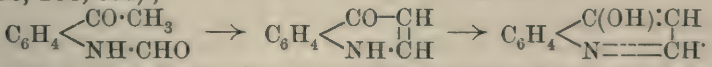
Methyl cinchomeronate chloride, $COCl\cdot C_5NH_3\cdot CO_2Me$, prepared from methyl hydrogen cinchomeronate, crystallises in silky needles melting and decomposing at 183°; with methyl alcohol, it gives the hydrochloride of the dimethyl ester, and with ammonia the diamide.

Pyridine-2 : 3 : 4-tricarboxylic acid reacts only slowly with thionyl chloride; the product yields, with methyl alcohol, the hydrochloride of a dimethyl ester. Dimethyl pyridine-2 : 3 : 4-tricarboxylate readily gives a crystalline chloride, which with methyl alcohol produces *trimethyl pyridine*-2 : 3 : 4-*tricarboxylate*, $C_5NH_2(CO_2Me)_3$; the latter compound crystallises in lustrous needles melting at 97°; the *hydrochloride* forms hygroscopic needles melting at 68°. *Triethyl pyridine*-2 : 3 : 4-*tricarboxylate*, prepared in a similar manner from the diethyl ester, is an oil boiling and decomposing at 300—305°; the hydrochloride crystallises in long, lustrous needles melting at 61°.

K. J. P. O.

Chloroiodohydroxyquinoline. BASLER CHEMISCHE FABRIK (D.R.-P. 117767).—*Chloroiodohydroxyquinoline*, is prepared by digesting a potassium hydroxide solution of 5-chloro-8-hydroxyquinoline with a solution of iodine in potassium iodide or a mixture of this salt with a hypochlorite; it crystallises from glacial acetic acid in yellowish-brown needles, melts at 177—178°, and is very sparingly soluble in water or alcohol. G. T. M.

Conversion of Aminophenylpropiolic Acid into Kynurenic Acid and Allied Compounds. By RUDOLF CAMPS (*Ber.*, 1901, **34**, 2703—2718; *Zeit. physiol. Chem.*, 1901, **33**, 390—411).—*Formyl-o-aminoacetophenone*, $CHO\cdot NH\cdot C_6H_4\cdot CO\cdot CH_3$, prepared by boiling *o*-aminoacetophenone with formic acid during 5 or 10 minutes only, crystallises from hot alcohol in minute, colourless, glistening needles and melts at 79°. It is readily hydrolysed by boiling with hydrochloric acid, but when boiled with sodium hydroxide is converted into 4-hydroxyquinoline, which was found to be identical with the kynurin first prepared by Schmiedeberg and Schulzen (*Annalen*, 1872, **164**, 155) by heating Liebig's kynurenic acid (*Annalen*, 1853, **86**, 125 1858, **108**, 354);

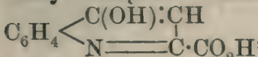


$$C_6H_4{<}\begin{array}{l}CO\cdot CH_3\\ NH\cdot CHO\end{array} \rightarrow C_6H_4{<}\begin{array}{l}CO-CH\\ \qquad\;\, \|\\ NH\cdot CH\end{array} \rightarrow C_6H_4{<}\begin{array}{l}C(OH){:}CH\\ \qquad\qquad\;\, |\\ N{=\!=\!=}CH\end{array}$$

o-Aminoacetophenone (2 mols.) combines at the ordinary temperature with ethyl oxalate (1 mol.) to form an *additive* product, $C_{22}H_{28}O_6N$, which crystallises from light petroleum in pale yellowish, glistening needles, melts at 42°, and is decomposed by acids. When heated together at 150—160°, *ethyloxalyl-o-aminoacetophenone*,

$$CH_3\cdot CO\cdot C_6H_4\cdot NH\cdot CO\cdot CO_2Et,$$

results, and by crystallising from hot alcohol is obtained in glistening needles melting at 128°. Under the action of sodium hydroxide, the oxalyl compound condenses to a 4-*hydroxyquinoline-2-carboxylic acid*,



$$C_6H_4{<}\begin{array}{l}C(OH){:}CH\\ \qquad\qquad\;\, |\\ N{=\!=\!=}C\cdot CO_2H\end{array},$$

which crystallises from dilute acetic acid in silky, felted needles, melts with liberation of carbon dioxide at 290°, and is converted into kynurin; the acid is isomeric with kynurenic acid, which must therefore be the 3-acid.

Ethyl formyl-o-aminophenylpropiolate, $CHO\cdot NH\cdot C_6H_4\cdot C\vdots C\cdot CO_2Et$, prepared by the action of formic acid on ethyl *o*-aminophenylpropiolate dissolved in ether, crystallises from alcohol in stout, colourless, silky needles, melts at 83°, and when boiled with sodium hydroxide in aqueous alcoholic solution is converted into kynurenic acid.

Ethyl acetyl-o-aminophenylpropiolate, $NHAc\cdot C_6H_4\cdot C\vdots C\cdot CO_2Et$, crystallises in minute needles, melts at 124°, and is converted by alkalis into 2-hydroxy-4-methylquinoline, a substance melting at 228°, and 4-hydroxyquinaldine-3-carboxylic acid. T. M. L.

Preparation of 2 : 4-Dihydroxyquinoline. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 117167).—A quantitative yield of 2 : 4-dihydroxyquinoline (γ-hydroxycarbostyril) is obtained when an alkali, calcium, or barium salt of acetylanthranilic acid is heated at 280—300° with dry potassium hydroxide or a mixture of this reagent and quicklime (compare D.R.-P. 102894). G. T. M.

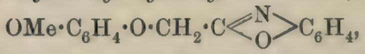
a-Dinitrophenylpyridine Chloride and the Product of its Transformation under the Influence of Alkali. By LEOPOLD SPIEGEL (*Ber.*, 1901, **34**, 3021—3024. Compare Abstr., 1900, i, 51).—[With KATZENELLENBOGEN.]—This investigation, although still incomplete, affords additional evidence in support of the author's view regarding the constitution of the product, $C_{11}H_9N_3O_5$, obtained from a-dinitrophenylpyridine chloride by the action of alkalis. This substance, when heated for some time with absolute alcohol, decomposes into pyridine and 2 : 4-dinitrophenyl ethyl ether ; this behaviour is in accordance with the suggested constitutional formula,

$$C_6H_3(NO_2)_2\cdot C_5NH_5\cdot OH.$$

G. T. M.

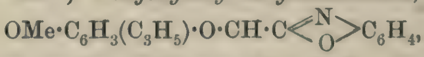
Condensation Products of Phenoxyacetic Acids with o-Aminophenol. By GEORG COHN (*J. pr. Chem.*, 1901, [ii], **64**, 293—296. Compare this vol., i, 352).—Phenoxyacetic acid and its derivatives condense with *o*-aminophenol at 170° to form highly coloured products, from which 1-phenoxymethylbenzoxazoles can be isolated. These substances readily dissolve in alkalis, the oxazole nucleus being broken and phenoxyacetaminophenols produced. Acids precipitate the benzoxazole from the alkaline solution ; if the alkaline solution is boiled, the last mentioned compounds are resolved into *o*-aminophenol and the phenoxyacetic acid.

1-*Phenoxymethylbenzoxazole*, $OPh\cdot CH_2\cdot C\genfrac{<}{>}{0pt}{}{N}{O}C_6H_4$, crystallises in needles and melts at 146—147° ; 1-p-*tolyloxymethylbenzoxazole* $C_6H_4Me\cdot O\cdot CH_2\cdot C\genfrac{<}{>}{0pt}{}{N}{O}C_6H_4$, melts at 142°—143° ; 1-*thymyloxymethylbenzoxazole*, $C_6H_3MePr\cdot O\cdot CH_2\cdot C\genfrac{<}{>}{0pt}{}{N}{O}C_6H_4$, crystallises in needles melting at 191—192 ; the *carvacryloxy*-compound forms leaflets melting at 195—197° ; 1-*guaiacyloxymethylbenzoxazole*,



$$OMe\cdot C_6H_4\cdot O\cdot CH_2\cdot C\genfrac{<}{>}{0pt}{}{N}{O}C_6H_4,$$

melts at 143—144° ; 1-*eugenyloxymethylbenzoxazole*,



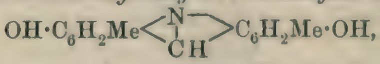
$$OMe\cdot C_6H_3(C_3H_5)\cdot O\cdot CH\cdot C\genfrac{<}{>}{0pt}{}{N}{O}C_6H_4,$$

crystallises in long needles melting at 111—113°.

a-*Naphthyloxymethylbenzoxazole*, $C_{10}H_7\cdot O\cdot CH_2\cdot C\genfrac{<}{>}{0pt}{}{N}{O}C_6H_4$, melts at 220°, and the *β-naphthyl* derivative at 204°.

K. J. P. O.

2 : 8-Dihydroxy-3 : 7-dimethylacridine. LEOPOLD CASSELLA (D.R.-P. 120466).—2 : 8-*Dihydroxy*-3 : 7-*dimethylacridine*,

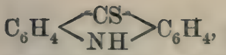


$$OH\cdot C_6H_2Me\genfrac{<}{>}{0pt}{}{N}{CH}C_6H_2Me\cdot OH,$$

produced by condensing 4-amino-*o*-cresol with formaldehyde in the presence of dilute sulphuric acid, separates from water in orange-coloured crystals ; it is slightly soluble in dilute acids, but readily dissolves in alkalis to an orange-yellow solution having an intense green fluorescence.

G. T. M.

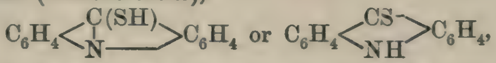
Thioacridone. KALLE & Co. (D.R.-P. 120586).—*Thioacridone*,



$C_6H_4\left\langle\begin{matrix}CS\\NH\end{matrix}\right\rangle C_6H_4$, prepared by fusing acridine with sulphur at 200°, melts at 271°, and dissolves in concentrated hydrochloric acid, yielding a crystalline hydrochloride. G. T. M.

Acridine. I. By Albert Edinger and W. Arnold (*J. pr. Chem.*, 1901, [ii], **64**, 182—198. Compare this vol., i, 166).—On heating acridine with sulphur monochloride under pressure at 270—280°, a *compound*, $C_{13}HNCl_6S_2$, is formed; it crystallises in deep red, insoluble needles melting at 306° and is of neutral character.

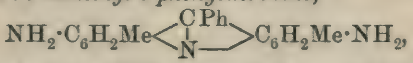
5-*Thioacridol* (5-*thioacridone*),



$$C_6H_4\left\langle\begin{matrix}C(SH)\\|\\N\end{matrix}\right\rangle C_6H_4 \text{ or } C_6H_4\left\langle\begin{matrix}CS\\NH\end{matrix}\right\rangle C_6H_4,$$

is produced when flowers of sulphur and acridine are heated under pressure at 190—195° and forms reddish-brown crystals melting at 275°; it also crystallises, with H_2O, in brownish-yellow needles and dissolves both in alkalis and acids, but not in solutions of carbonates; the *hydrochloride* crystallises in greenish-yellow needles, which rapidly lose hydrogen chloride. 5-Thioacridol is readily benzoylated by the Schotten-Baumann method and forms a benzyl thioether with benzyl chloride, which by alcoholic hydrogen chloride is converted into acridone and benzyl mercaptan; with methyl iodide, a methyl thioether is obtained; oxidising agents produce acridone. From the solution of thioacridol in dilute nitric acid, ammonia precipitates a strongly basic substance containing sulphur; if the solution in nitric acid is heated, sulphuric acid and a mixture of acridone and nitrated acridone are formed. K. J. P. O.

Preparation of Acridine Colouring Matters by means of Benzaldehyde. Badische Anilin- & Soda-Fabrik (D.R.-P. 118075).—2 : 8-*Diamino*-3 : 7-*dimethyl*-5-*phenylacridine*,

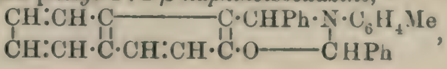


$$NH_2{\cdot}C_6H_2Me\left\langle\begin{matrix}CPh\\|\\N\end{matrix}\right\rangle C_6H_2Me{\cdot}NH_2,$$

prepared by heating at 120—160° benzylidene-2 : 4-tolylenediamine with a mixture of *p*-toluidine and its hydrochloride, is a brown powder sparingly soluble in water. G. T. M.

Condensation between β-Naphthol, Aldehydes, and Amines. III. By Mario Betti (*Gazzetta*, 1901, **31**, ii, 170—184. Compare this vol., i, 81 and 611).—The main bulk of the product obtained by the interaction of β-naphthol with an amine and an aldehyde, consists of an oxazine derivative, but a secondary product is also formed, which, in the case of benzylamine, has been separated in quantity sufficient to allow of its properties being studied. The latter compound is formed from 1 mol. each of β-naphthol, aldehyde, and base, with the elimination of $1H_2O$; it gives a diacetyl derivative, and is perfectly analogous to the additive products obtained from aldehydoaminic bases and naphthols (compare Betti, this vol., i, 81).

1 : 3-*Diphenyl*-2-p-*tolyl*-4 : 2-β-*naphtho*iso*oxazine*,



$$\begin{array}{l} CH{:}CH{\cdot}C\text{————}C{\cdot}CHPh{\cdot}N{\cdot}C_6H_4Me \\ \;| \qquad\quad\;\, \| \qquad\qquad\quad\;\, \| \qquad\qquad\;\; | \\ CH{:}CH{\cdot}C{\cdot}CH{:}CH{\cdot}C{\cdot}O\text{——}CHPh \end{array},$$

prepared from β-naphthol, benzaldehyde, and *p*-toluidine, separates from a mixture of benzene and light petroleum as a white, crystalline powder, which begins to turn yellow at 190° and melts at 205°; with ferric chloride solution, it gives no colour in the cold, but on warming, the liquid becomes intensely reddish-violet

1 : 3-*Diphenyl-2-benzyl*-4 : 2-*β-naphtho*iso*oxazine*, $C_{31}H_{25}ON$, obtained from β-naphthol, benzaldehyde, and benzylamine, is deposited from a mixture of benzene and light petroleum as a white, crystalline powder melting at 187°. It is not changed by cold ferric chloride solution, but on heating the liquid assumes a ruby-red coloration, which disappears on cooling. It forms an *acetyl* compound, $C_{31}H_{24}ONAc$, which separates in rosettes of small, white crystals melting at 190°; with ferric chloride, it behaves like the parent substance.

Benzylidene-benzylamine-β-naphthol, $CH_2Ph{\cdot}NH{\cdot}CHPh{\cdot}C_{10}H_6{\cdot}OH$, also obtained from β-naphthol, benzaldehyde, and benzylamine, crystallises from 90 per cent. alcohol in large, shining needles melting at 145°. With cold ferric chloride solution, it gives a dark violet coloration. Its *diacetyl* derivative, $C_{28}H_{25}O_3N$, is deposited from alcohol in yellow, spherical, crystalline aggregates melting at 166°; with ferric chloride solution, it gives no coloration, even on boiling. It reacts with benzaldehyde, giving 1 : 3-diphenyl-2-benzyl-4 : 2-β-naphtho*iso*oxazine.

The interaction of β-naphthol, benzaldehyde, and amylamine gives rise to:

(1) 1 : 3-*Diphenyl-2-amyl*-4 : 2-*β-naphtho*iso*oxazine*, $C_{29}H_{29}ON$, which separates from alcohol in small, rhomboidal crystals; these melt at 141° and with ferric chloride solution give, on warming, a reddish-violet coloration which disappears on cooling.

(2) *Benzylidene-amylamine-β-naphthol*, $C_5H_{11}{\cdot}NH{\cdot}CHPh{\cdot}C_{10}H_6{\cdot}OH$, which crystallises from alcohol in long, white needles melting at 120°; with ferric chloride solution, it gives, in the cold, an intense dark violet coloration.

1 : 3-*Diphenyl-2-ethyl*-4 : 2-*β-naphtho*iso*oxazine*, $C_{26}H_{23}ON$, obtained by the interaction of β-naphthol, benzaldehyde, and ethylamine, crystallises from alcohol in hard, sparkling scales melting at 146° and on heating with ferric chloride solution gives a red coloration.

1 : 3-*Diphenyl-2-methyl*-4 : 2-*β-naphtho*iso*oxazine*, $C_{25}H_{21}ON$, prepared from β-naphthol, benzaldehyde, and methylamine, crystallises from alcohol in yellowish needles melting at 137°; with ferric chloride solution, it gives a red coloration only on heating. T. H. P.

Two New Nitroaminodiphenylamines. By FREIDRICH KEHRMANN and G. STEINER (*Ber.*, 1901, **34**, 3089—3092).—When heated for 7 hours at 170—180°, *o*-chloronitrobenzene condenses with *m*-phenylenediamine, forming 2-*nitro-3′-aminodiphenylamine*, which crystallises in long red needles from alcohol, melts at 112°, and forms a *sulphate* crystallising in yellow needles or prisms; the corresponding 2 : 3′-*diaminodiphenylamine*, obtained by the reduction of the nitro-compound, forms a colourless *hydrochloride*, which crystallises in concentric groups of needles.

2-*Nitro-2′-aminodiphenylamine*, obtained in small quantities along with diaminophenazine and fluorindine by the condensation of *o*-chloronitrobenzene and *o*-phenylenediamine, crystallises in yellowish-red needles and melts at 103°. R. H. P.

Nitro-*m*-phenylenediaminesulphonic Acid. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 120345).—1 : 3-*Dichloro*-6-*nitrobenzene*-4-*sulphonic acid*, prepared by sulphonating *m*-dichlorobenzene with fuming sulphuric acid (23 per cent. SO_3) and nitrating the product with a mixture of this acid and concentrated nitric acid, separates out from the mixture on the addition of water in pale yellow needles. 6-*Nitro*-1 : 3-*phenylenediamine*-4-*sulphonic acid*, obtained by heating the dichloro-compound with 30 per cent. ammonia solution at 150°, crystallises from water in yellow, silky needles sparingly soluble in hydrochloric acid. The lead and potassium salts crystallise in yellow needles.
G. T. M.

Di-*p*-substituted Diphenylamine Derivatives with free Ortho-positions. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 117891. Compare D.R.-P. 112180).—p-*Amino*-p-*hydroxyphenyl*-m-*tolylamine*, $NH_2\cdot C_6H_4\cdot NH\cdot C_6H_3Me\cdot OH$, is readily prepared by condensing *p*-nitrobenzenesulphonic acid with *p*-aminocresol, reducing the product, and heating the resulting aminosulphonic acid, $NH_2\cdot C_6H_3(SO_3H)\cdot NH\cdot C_6H_3Me\cdot OH$, with 60 per cent. sulphuric acid; it crystallises in white needles melting at 166°. G. T. M.

***p*-Dihydroxydiphenyl-4 : 6-dinitro-1 : 3-phenylenediamine.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 121211).—p-*Dihydroxydiphenyl*-4 : 6-*dinitro*-1 : 3-*phenylenediamine*,

$$(NO_2)_2C_6H_2(NH\cdot C_6H_4\cdot OH)_2,$$

produced by heating 1 : 3-dichloro-4 : 6-dinitrobenzene (1 mol.) and *p*-aminophenol (2 mols.) with sodium acetate and alcohol, crystallises in red plates and melts at 284—286°. Its *disulphonic* acid,

$$(NO_2)_2C_6H_2[NH\cdot C_6H_3(OH)\cdot SO_3H]_2,$$

obtained by substituting for *p*-aminophenol its sulphonic acid, forms yellowish-red crystals soluble in water and precipitated by sodium chloride. The corresponding *dicarboxylic* acid,

$$(NO_2)_2C_6H_2[NH\cdot C_6H_3(OH)\cdot CO_2H]_2,$$

prepared from aminosalicylic acid and 1 : 3-dichloro-4 : 6-dinitrobenzene, is a yellow powder insoluble in water and only slightly soluble in alcohol, benzene, or glacial acetic acid. G. T. M.

Oxygen Ethers of the Carbamides. Methyl- and Ethyl-*iso*carbamide. By RALPH H. MCKEE (*Amer. Chem. J.*, 1901, **26**, 209—264. Compare Stieglitz and McKee, Abstr., 1899, i, 594; 1900, i, 340, 431).—*Phenylethyl*isocarbamide (*ethyl iminophenylcarbamate*), $NH_2\cdot C(OEt){:}NPh$ or $NH{:}C(OEt)\cdot NHPh$, obtained by passing dry hydrogen chloride into a well-cooled alcoholic solution of phenylcyanamide, is a colourless liquid of amine-like odour, which boils at 138—139·5° under 18 mm. pressure, does not solidify at −15°, has n_D 1·5575 at 23°, and is readily soluble in the usual organic solvents; it dissolves sparingly in water, forming a strongly alkaline solution. It is not affected by exposure to the air or by boiling water, but if heated with water in a sealed tube it is slowly decomposed. When heated with hydrogen chloride, it yields ethyl chloride and phenylcarbamide. The *hydrochloride* crystallises from water in groups of long needles and melts and decomposes at 110°. The *platinichloride* forms dark yellow plates and melts and decomposes at 160°.

Phenylguanidine does not possess the properties ascribed to it by Feuerlein (Abstr., 1880, 44). By heating a mixture of cyanamide, aniline hydrochloride, and alcohol in a sealed tube for $2\frac{1}{2}$ hours at 100°, it is obtained as a hygroscopic, crystalline solid, which melts at 66°, absorbs carbon dioxide from the air, and undergoes decomposition when strongly heated in a vacuum. The *platinichloride* melts and decomposes at 197—198°. The *dibenzoyl* derivative crystallises in needles and melts at 183·5°. The picrate melts at 221°.

By the action of aniline on phenylethyl*iso*carbamide at 175° in a sealed tube, phenylcarbamide, ethylaniline, and ethylamine are produced. When an ethereal solution of phenylethyl*iso*carbamide is treated with benzoyl chloride, an oily mixture of two isomeric *benzoyl* derivatives is obtained, which slowly deposits slender prisms; when this oily mixture is heated with hydrochloric acid, ethyl chloride, benzoylphenylcarbamide, and benzanilide are formed.

*Phenylmethyl*iso*carbamide* (*methyl phenyliminocarbamate*),

$$\mathrm{NH{:}C(OMe){\cdot}NHPh},$$

obtained by the action of hydrogen chloride on a solution of phenylcyanamide in methyl alcohol, boils at 124° under 10 mm., 133° under 15 mm., and 140° under 23 mm. pressure; it forms a crystalline solid which melts at 46·5° and has a fishy odour and bitter taste. If it is heated with dilute hydrochloric acid, ethyl chloride and phenylcarbamide are produced. The *hydrochloride* melts and decomposes at 90°. The *sulphate* crystallises in plates and melts at 139°. By the action of benzoyl chloride on phenylmethyl*iso*carbamide, two isomeric compounds are produced. The s-*benzoyl* derivative, $\mathrm{NHBz{\cdot}C(OMe){:}NPh}$, is obtained as an oil which is decomposed by hydrogen chloride with formation of methyl chloride and *s*-benzoylphenylcarbamide; it yields salts with both bases and acids. The as-*benzoyl* derivative, $\mathrm{NBzPh{\cdot}C(OMe){:}NH}$, is a crystalline solid which melts at 64—65°, and, like the *s*-derivative, forms potassium and silver salts; when heated with dry hydrogen chloride, methyl chloride is evolved and crystals of as-*benzoylphenylcarbamide* melting at 146° are produced. *Diphenylmethyl*iso*biuret*,

$$\mathrm{NHPh{\cdot}C(OMe){:}N{\cdot}CO{\cdot}NHPh},$$

obtained by the action of phenylcarbimide on phenylmethyl*iso*carbamide, is a crystalline substance which melts at 111° and is soluble in chloroform, alcohol or ether; when the *hydrochloride* is heated in a vacuum, methyl chloride and α-diphenylbiuret are produced.

o-*Tolylethyl*iso*carbamide* (*ethyl* o-*tolyliminocarbamate*),

$$\mathrm{NH_2{\cdot}C(OEt){:}N{\cdot}C_7H_7},$$

obtained by the action of hydrogen chloride on an alcoholic solution of *o*-tolylcyanamide, boils at 144° under 19 mm. pressure and has not been solidified; it is decomposed by dry hydrogen chloride with formation of ethyl chloride and *o*-tolylcarbamide melting at 190°. The *platinichloride* crystallises in hexagonal prisms and melts and decomposes at 177°.

When *as*-phenylmethylethyl*iso*carbamide is heated with dilute hydrochloric acid, ethyl chloride and *as*-phenylmethylcarbamide are produced, together with some methylaniline and methylethylaniline.

*a-Diphenyl-a-methylethyl*iso*biuret*, $NPhMe\cdot C(OEt){:}N\cdot CO\cdot NHPh$, obtained by the action of phenylcarbimide on phenylmethylethyl*iso*carbamide, melts at 115—116°, and when boiled with dilute hydrochloric acid yields ethyl chloride and *a*-diphenyl-*a*-methylbiuret melting at 101—102°.

as-*Phenyldimethyl*iso*carbamide* (*methyl iminophenylmethylcarbamate*), $NPhMe\cdot C(OMe){:}NH$, boils at 120° under 11 mm. pressure.

*Benzoylmethyl*iso*carbamide* (*methyl iminobenzoylcarbamate*),

$$NHBz\cdot C(OMe){:}NH,$$

crystallises in monoclinic prisms, melts at 76·5°, and has both basic and acidic properties; when it is heated with dilute hydrochloric acid, methyl chloride, benzoylcarbamide, benzoic acid, and methylamine are produced.

*Phenylmethyl*iso*biuret* (*methyl phenylureidoiminoformate*),

$$NHPh\cdot CO\cdot N{:}C(OMe)\cdot NH_2,$$

obtained by the action of phenylcarbimide on methyl*iso*carbamide, crystallises in four-sided prisms with blunt pyramidal ends and melts at 89·5—90°; the *hydrochloride* melts and decomposes at 133°. When phenylmethyl*iso*biuret is boiled with dilute hydrochloric acid, methyl chloride is evolved and *a-phenylbiuret*, which melts at 156—156·5° and is soluble in alcohol or hot water, is produced.

Ethyl*iso*carbamide *hydrochloride* melts at 123—124°, evolving ethyl chloride. The *platinichloride* crystallises in four-sided, dark yellow plates and melts and decomposes at 178·5°. By the action of dilute hydrochloric acid on ethyl*iso*carbamide, ethyl chloride, carbamide, and a small quantity of ethylurethane are produced.

*Phenylethyl*iso*biuret* (*ethyl phenylureidoiminoformate*),

$$NHPh\cdot CO\cdot NH\cdot C(OEt){:}NH,$$

crystallises in monoclinic prisms, melts at 85·5—86°, and when heated with dilute hydrochloric acid yields ethyl chloride and phenylbiuret; the *hydrochloride* melts and decomposes at 141°.

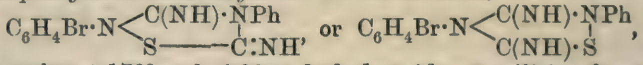
Comparative determinations of the hydrolysis of the hydrochlorides of ethyl iminobenzoate and phenyl ethyl*iso*carbamide show that the former is hydrolysed by water in approximately $N/12$ concentration to the extent of rather less than 1 per cent., whilst the hydrochlorides of phenylethyl- and phenylmethyl-*iso*carbamides are not hydrolysed at all at this concentration, and further that whilst ethyl iminobenzoate is a fairly strong base, easily undergoing ionisation, phenylethyl*iso*carbamide is a still stronger base, the affinity constant of which is probably close to that of potassium or sodium hydroxide. E. G.

Action of Halogens on Thiocarbamides. By A. HUGERSHOFF (*Ber.*, 1901, **34**, 3130—3135).—Phenylcarbamide in chloroform solution interacts with bromine in its isodynamic form, $SH\cdot C(NH_2){:}NPh$, giving hydrogen bromide and *carbaminophenyliminodisulphide tetrabromide* (*bromocarbaminophenylbromoaminodisulphide*), $S_2[CBr(NH_2)\cdot NPhBr]_2$, which melts and decomposes at about 208°, gradually loses bromine on exposure to the air, and is reduced by sulphurous acid solution to *carbaminophenyliminodisulphide*, $S_2[C(NH_2){:}NPh]_2$; this crystallise from water in nacreous leaflets, melts at 128°, and yields a well-defined *hydrochloride* melting at 236° and a crystalline platinichloride. The tetrabromide dissolves in water, yielding a mixture of carbaminophenyliminodisulphide and its *bromo*-derivative, $S_2[C(NH_2){:}N{\cdot}C_6H_4Br]_2$, formed as follows,

$$S_2[CBr(NH_2){\cdot}NPhBr]_2 \longrightarrow S_2[CBr(NH_2){\cdot}NH{\cdot}C_6H_4Br]_2 \longrightarrow S_2[C(NH_2,HBr){:}N{\cdot}C_6H_4Br]_2;$$

by a transformation common to the bromoamino-bases the *hydrobromide* of the base forms white needles and melts at 261—263°.

In alcoholic solution, phenylthiocarbamide yields with bromine a *bromodiphenyldi-iminotetrahydro*-1 : 2 : 4-*thiodiazole*,



$$C_6H_4Br{\cdot}N{<}\begin{matrix}C(NH){\cdot}NPh\\ |\\ S{-\!-\!-}C{:}NH\end{matrix} \text{ or } C_6H_4Br{\cdot}N{<}\begin{matrix}C(NH){\cdot}NPh\\ |\\ C(NH){\cdot}S\end{matrix},$$

which melts at 172° and yields a *hydrobromide* crystallising from water and melting at 242—244°. As this compound cannot be obtained by brominating carbaminophenyliminodisulphide in alcohol, the latter is obviously not an intermediate product in the action. W. A. D.

Action of Bromine on Acetyldiphenylthiocarbamide in Chloroform Solution. By A. HUGERSHOFF and W. CHR. KÖNIG (*Ber.*, 1901, **34**, 3136—3142).—The action of bromine on acetyldiphenylthiocarbamide in chloroform solution gives rise to hydrogen bromide and a nearly theoretical quantity of the *bromide*,

$$NPhBr{\cdot}C(SBr_2){\cdot}NPhAc,$$

which forms orange-coloured crystals, melts and decomposes at 167°, and is converted by aqueous sodium hydroxide or sulphurous acid into the *sulphoxide*, $NHPh{\cdot}C(SO){\cdot}NPhAc$; the latter is remarkably stable and is not changed by alkaline lead hydroxide, mercuric oxide, concentrated sulphuric acid, alcoholic potassium hydroxide, or sodium amalgam. Water, unlike dilute alkali, converts the foregoing bromide into the *bromosulphoxide*, $C_6H_4Br{\cdot}NH{\cdot}C(SO){\cdot}NPhAc$, the bromine of the bromophenylamino-radicle wandering into the phenyl nucleus (compare preceding abstract); the product crystallises from alcohol in small, colourless needles, melts at 165° and is stable towards alkaline lead hydroxide, alkalis, and acids. W. A. D.

Phenacylidenebenzamidine and some Homologues. By FRANZ KUNCKELL and R. BAUER (*Ber.*, 1901, **34**, 3024—3029. Compare this vol., i, 294).—Phenacylidenebenzamidine is a weak base and yields a *hydrochloride*, $NH{:}CPh{\cdot}N{:}CH{\cdot}COPh,HCl$, and a *sulphate* crystallising in needles and melting respectively at 310° and 193°; the *platinichloride* forms yellow crystals and decomposes on heating. The *phenylhydrazone*, $NH{:}CPh{\cdot}N{:}CH{\cdot}CPh{:}N{\cdot}NHPh$, melts at 181°; the *silver* derivative, $NAg{:}CPh{\cdot}N{:}CH{\cdot}COPh$, formed by the interaction of the imino-base with ammoniacal silver nitrate, is a voluminous white precipitate, becoming dark on exposure to light. The *ethiodide*, $C_{17}H_{17}ON_2I$, separates from alcoholic solutions in white crystals melting at 180°.

p-*Tolacylidenebenzamidine*, $NH{:}CPh{\cdot}N{:}CH{:}CO{\cdot}C_6H_4Me$, prepared from benzamidine and *p*-tolyl dibromomethyl ketone, crystallises from alcohol in white leaflets melting at 254°; the *hydrochloride* melts at 316° and the *phenylhydrazone* at 176°; the *platinichloride* separates in small crystals and decomposes without melting. The *silver* derivative is a white, insoluble, flocculent compound, the *ethiodide* forms white crystals melting at 218°; the latter substance, on treatment with a dilute alcoholic solution of potassium hydroxide, yields the *ethyl* derivative, $NEt{:}CPh\cdot N{:}CH\cdot CO\cdot C_6H_4Me$; this product, which is also obtained by the action of ethyl iodide on the silver derivative, separates in white crystals and melts at 257°.

*Phenacylidene-*p*-tolenylamidine*, $NH{:}C(C_6H_4Me)\cdot N{:}CH\cdot COPh$, produced by the interaction of *p*-tolenylamidine and dibromoacetophenone in dry ether, forms white crystals melting at 220°; the *hydrochloride* separates in white needles and melts at 111°.

p-*Tolacylidene-*p*-tolenylamidine*, $NH{:}C(C_6H_4Me)\cdot N{:}CH\cdot CO\cdot C_6H_4Me$, prepared in a similar manner to the preceding base, melts at 240°.

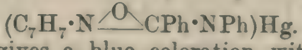
G. T. M.

Action of Benzamidine on Certain Aromatic Aldehydes. By FRANZ KUNCKELL and R. BAUER (*Ber.*, 1901, **34**, 3029—3032).—*Benzylidenebenzamidine*, $NH{:}CPh\cdot N{:}CHPh$, is readily obtained by adding benzaldehyde or benzylidene chloride to benzamidine dissolved in dry chloroform and then heating the mixture on the water-bath for 2—3 hours; it crystallises in colourless needles, melts at 175°, and yields a white, insoluble, *silver* derivative; its *hydrochloride* melts at 274°.

o-*Hydroxybenzylidenebenzamidine*, $NH{:}CPh\cdot N{:}CH\cdot C_6H_4\cdot OH$, melts at 185°; its *hydrochloride* and *platinichloride* melt respectively at 155° and 215°, the *silver* derivative is a white, insoluble compound. Benzoylformaldehyde readily interacts with benzamidine, yielding the compound $NH{:}CPh\cdot CH\cdot COPh$. G. T. M.

Hydroxyamidines. By HEINRICH LEY (*Ber.*, 1901, **34**, 2620—2631. Compare Abstr., 1898, i, 252).—*αβ-Diphenyl-γ-benzylhydroxyamidine*, $NPh{:}CPh\cdot N(C_7H_7)\cdot OH$ (*loc. cit.*), which melts at 150°, possesses feeble acid properties and also somewhat stronger basic properties. The *hydrochloride* crystallises in sparingly soluble needles and melts and decomposes at 194°. The aqueous solution has an acid reaction and it may be calculated from the electrical conductivity that this salt is hydrolysed in aqueous solution to four times the extent of aniline hydrochloride. The *platinichloride* forms brown, octahedral crystals and the *cobalt* and *nickel* salts are both crystalline. The *mercury* salt, $Hg(C_{20}H_{17}ON_2)_2$, crystallises in yellow needles and is not decomposed by aqueous sodium hydroxide. It forms a double salt with mercuric acetate,

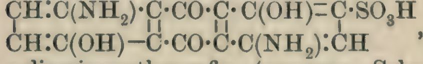
$$Hg(C_{20}H_{17}ON_2)_2,Hg(C_2H_3O_2)_2,$$

which crystallises in light yellow needles melting at 142°. From a solution of this salt, sodium hydroxide precipitates only the mercuric oxide corresponding with the mercuric acetate. It seems probable that the metallic compounds belong to two different types, the easily decomposed sodium salt may have the formula $NPh{:}CPh\cdot N(ONa)C_7H_7$, whilst the stable mercury salt probably contains the metal united to nitrogen,  $(C_7H_7\cdot N\overset{O}{\frown}CPh\cdot NPh)Hg$. The alcoholic solution of the amidine gives a blue coloration with ferric chloride and a greenish-black coloration with manganese acetate. The *benzyl ether* crystallises in small needles melting at 99° and gives no coloration with ferric chloride. On one occasion, a second product of benzylation was obtained which melted at 163°. The *picryl ether*, $C_{26}H_{19}O_7N_5$, is obtained by the action of picryl chloride in alcoholic solution and forms orange-red crystals with a green surface lustre, which melt and decompose suddenly at 130—131°. The chloroform solution exhibits a strong green fluorescence, whilst the alcoholic solution is only faintly fluorescent, and this behaviour appears to be characteristic of the hydroxyamidines. *β-Phenyl-α-o-tolyl-γ-benzylhydroxyamidine* forms a *copper* salt, $(C_{21}H_{19}ON_2)_2Cu$, which crystallises in bronze coloured plates. *β-Phenyl-α-m-nitrophenyl-γ-benzylhydroxyamidine* crystallises in golden coloured needles melting at 171° and shows all the characteristic reactions. The *copper* salt forms brownish-red plates, the *cobalt* salt crystallises in microscopic, brown needles, and the *nickel* salt is an orange-yellow, crystalline precipitate. *Benzoyl-m-nitroanilideiminochloride*, from which the foregoing hydroxyamidine is prepared, crystallises in tablets melting at 80—82°.

β-Phenyl-γ-benzyl-αβ-naphthylhydroxyamidine crystallises in yellowish needles melting at 175° and forms characteristic *copper* and *cobalt* salts. A. H.

1 : 7-Diamino-2-hydroxynaphthalene. LEOPOLD CASSELLA & Co. (D.R.-P. 117298).—1 : 7-*Diamino-2-hydroxynaphthalene*, prepared by reducing either the azo-compound, obtained by adding benzenediazonium chloride to an alkaline solution of 7-amino-β-naphthol, or the product of the action of nitrous acid on the same amino-compound, crystallises in lustrous leaflets melting at 220° and differs from the diaminonaphthol previously described (Abstr., 1890, 1424) in yielding a violet solution with nitrous acid, whereas the isomeride develops a reddish-brown coloration. G. T. M.

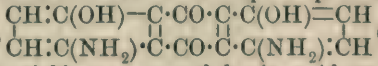
[Diaminodihydroxyanthraquinonesulphonic Acid.] FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 117892).—A *diaminodihydroxyanthraquinonesulphonic acid* having the following constitution,



$$\begin{array}{l}\mathrm{CH{:}C(NH_2)\cdot C\cdot CO\cdot C\cdot C(OH){=}C\cdot SO_3H}\\ \mathrm{CH{:}C(OH){-}C\cdot CO\cdot C\cdot C(NH_2){:}CH}\end{array}$$

, is prepared by sulphonating *p*-diaminoanthrarufin (compare Schmidt and Gattermann, Abstr., 1897, i, 197) with fuming sulphuric acid (5 per cent. SO_3) or chlorosulphonic acid; it is obtained as a dark powder sparingly soluble in cold water. The acid yields a well characterised pyridine salt and dyes wool blue either with or without a mordant. G. T. M.

[*p*-Diaminochrysazinsulphonic Acid.] FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 117893. Compare preceding abstract).—*p*-Diaminochrysazin,



$$\begin{array}{l}\mathrm{CH{:}C(OH){-}C\cdot CO\cdot C\cdot C(OH){=}CH}\\ \mathrm{CH{:}C(NH_2)\cdot C\cdot CO\cdot C\cdot C(NH_2){:}CH}\end{array}$$

(compare D.R.-P. 98639 and 100138), yields a *monosulphonic acid* on treatment with fuming sulphuric acid; this substance dyes wool blue either with or without a mordant (compare Eng. Pat. 7291 of 1900). G. T. M.

The Three Isomeric β-Aminophenylbenziminoazoles. By BOL. MIKLASZEWSKI and STEFAN VON NIEMENTOWSKI (*Ber.*, 1901, **34**, 2953—2974. Compare Abstr., 1899, i, 643).—The β-aminophenylbenziminoazoles are colourless crystalline compounds insoluble in water, but readily soluble in organic media. They are decided bases, yielding well-defined salts with two equivalents of an acid, the nitrates and hydrochlorides being readily soluble in water or alcohol. The acetyl derivatives of the meta- and para-compounds do not yield cyclic di-anhydrides, and in this respect differ from the ortho-compound. Both acetyl and benzoyl derivatives are indifferent substances and only sparingly soluble in organic solvents. On treatment with alcoholic hydrogen sulphide, the *m*- and *p*-iminoazoles yield thiocarbamide derivatives, which are yellow in colour and soluble in alkalis.

All three iminoazoles may be diazotised in strongly acid solution at 0°, and the diazo-salts thus obtained, when added to alkaline β-naphthol solution, yield characteristic red dyes, and when reduced with stannous chloride, form yellow hydrazines soluble in alkalis and acids, but only sparingly so in organic solvents. These hydrazines reduce ammoniacal silver nitrate but not Fehling's solution, and yield hydrazones with aldehydes, ketones, and ketonic acids.

m-*Nitrobenzoyl-*o*-nitroanilide,* $NO_2\cdot C_6H_4\cdot NH\cdot CO\cdot C_6H_4\cdot NO_2$, forms pale yellow needles melting at 138°, dissolves in concentrated mineral acids, also in alkalis, and unlike the *o*-compound does not change colour on exposure to light. β-m-*Aminophenylbenziminoazole* melts at 251—252°; the *hydrochloride,* $C_{13}H_{11}N_3,2HCl$, forms prismatic crystals melting at 328°, the *nitrate,* $C_{13}H_{11}N_3,HNO_3$, melts and decomposes at 265—270°. The *acetyl* derivative, $C_6H_4\genfrac{<}{>}{0pt}{}{N}{NH}C\cdot C_6H_4\cdot NHAc$, crystallises from alcohol in short, colourless needles melting at 288° and is only sparingly soluble in acetone, benzene, or toluene. The *benzoyl* derivative, $C_{20}H_{15}ON_3$, forms compact crystals melting and decomposing at 139°. The *thiocarbamide* derivative, $C_{27}H_{20}N_6S$, forms a yellow, amorphous mass. β-*Naphthol*-β-m-*azophenylbenziminoazole,* $C_{23}H_{16}ON_4$, is a bright scarlet-red powder melting at 156—157° and insoluble in water, but soluble in alkalis. The isomeric o-*compound* forms a brick-red powder melting at 272°; this dye is not formed so readily as its two isomerides.

β-o-*Hydrazinophenylbenziminoazole,* $C_6H_4\genfrac{<}{>}{0pt}{}{N}{NH}C\cdot C_6N_4\cdot NH\cdot NH_2$, crystallises from alcohol in yellow, rhombic plates melting and decomposing at 182° and is only sparingly soluble in ether or water; the *hydrochloride,* $C_{13}H_{12}N_4,2HCl$, forms yellow, glistening needles melting at 248°, and the *nitrate,* with $2HNO_3$, dark brown prisms melting and decomposing at 136°. The isomeric m-*hydrazino*-compound forms yellow plates melting between 245° and 258°, the *hydrochloride* melts at 256—257°, and the *nitrate* decomposes and melts at 145°.

p-Nitrobenzoyl-*o*-nitroanilide melts at 216°; Kym (this vol., i, 47) gives 219—220° as the melting point. The corresponding benziminoazole melts at 240° (235—236° Kym); the *hydrochloride,* $C_{13}H_{11}N_3,2HCl$, melts and decomposes at 348°, and the *nitrate,* $C_{13}H_{11}N_3,HNO_3$, between 215° and 230°; the *acetyl* derivative crystallises in short, thick needles melting at 299°; the *benzoyl* derivative forms rhombic plates or needles melting at 333°; the *thiocarbamide,* $C_{27}H_{20}N_6S$, forms crystalline rods melting and decomposing at

236—237°. *β-Naphthol-β-*p*-azophenylbenziminoazole* crystallises in red needles melting at 297—298°. *β-*p*-Hydrazinophenylbenziminoazole* melts and decomposes at 305°; the *hydrochloride*, with 2HCl, crystallises in yellow needles melting at 190—191°.

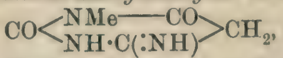
The following hydrazones have been prepared:

β-Phenylbenziminoazole hydrazone.

	Ortho.	Meta.	Para.
Benzaldehyde	melts and decomposes at 180°.	Yellow crystals, softens at 170°, begins to decompose at 200°.	Softens at 100°, decomposes at 120°
Pyruvic acid	Decomposes between 120° and 180°	Stout needles, softens at 184°, melts and decomposes at 195°.	Yellow needles, softens at 193°, decomposes at 220°.
Acetophenone	Pale yellow prisms, softens at 102°, melts at about 135°.	Not definitely crystalline, begins to decompose at 180°.	Yellow, begins to decompose at 148°.

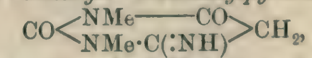
β-8-Quinolinebenziminoazole (Abstr., 1899, i, 647) forms a *hydrochloride*, $C_{16}H_{11}N_3,2HCl$, which crystallises in pale grey needles melting at 260°. β-5-(or 7-)*Quinolinebenziminoazole* crystallises, with $1H_2O$, in small needles, softens at 100—105°, and melts at 135—136°; it dissolves readily in most organic solvents and in mineral acids; the *hydrochloride*, with 2HCl, softens at 229° and melts at 236°, the *nitrate* with $2HNO_3$, forms long needles melting and decomposing at 196°. β-6-*Quinolinebenziminoazole* crystallises, with $1H_2O$, in pale grey needles melting at 105°; the anhydrous compound melts at 218°, the *hydrochloride* melts at 180—181°, and the *nitrate* melts and decomposes at 223—224°. J. J. S.

Cyclic Carbamides [Pyrimidines]. WILHELM TRAUBE (D.R.-P. 117922).—*Cyanoacetylmethylcarbamide*, produced by condensing cyanoacetic acid and methylcarbamide in the presence of phosphorus oxychloride, melts at 205°. *Iminomalonylmethylcarbamide* (4-*imino*-2 : 6-*dioxy*-1-*methylpyrimidine*),



$CO\left<\begin{matrix}NMe\text{——}CO\\NH\cdot C(:NH)\end{matrix}\right>CH_2$,

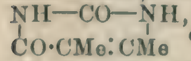
a colourless crystalline substance resulting from a rearrangement of the preceding compound under the influence of solutions of the alkali hydroxides, decomposes without melting and yields a purple iso*nitroso*-derivative, $C_5H_6O_3N_4$, on treatment with nitrous acid. *Iminomalonyldimethyl carbamide* (4-*imino*-2 : 6-*dioxy*-1 : 3-*dimethylpyrimidine*),



$$CO\left<\begin{matrix}NMe\text{——}CO\\NMe\cdot C(:NH)\end{matrix}\right>CH_2,$$

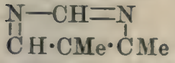
crystallises from water and yields a purple iso*nitroso*-compound, $C_6H_8O_3N_4$ (compare Mulder, Abstr., 1879, 618). G. T. M.

4 : 5-Dimethylpyrimidine. By JULIUS SCHLENKER (*Ber.*, 1901, **34**, 2812—2829).—2 : 6-*Dioxy*-4 : 5-*dimethylpyrimidine* (4 : 5-dimethyluracil),



$\begin{matrix}NH\text{—}CO\text{—}NH,\\|\qquad\qquad|\\CO\cdot CMe:CMe\end{matrix}$

obtained by heating iminodimethyluracil with hydrochloric acid under pressure, crystallises in pointed rods, melts at

290°, can be distilled, and, when treated with phosphorus oxychloride, is converted into the corresponding 2 : 6-*dichloro*-4 : 5-*dimethylpyrimidine*, which crystallises in long plates, melts at 70—71°, boils at 249—250°, and dissolves readily in most solvents. 4 : 5-*Dimethylpyrimidine*,  $\begin{matrix}\text{N—CH=N}\\ \| \qquad\quad | \\ \text{CH·CMe·CMe}\end{matrix}$, obtained from the dichloro-compound by treatment with zinc dust and water, crystallises in needles melting at 3°, boils at 176·5—177°, has a quinoline-like odour, gives a neutral solution in water, and forms a yellow, crystalline *platinichloride*, $(C_6H_8N_2)_2,PtCl_4$, which melts and decomposes at 242—243°, an *aurichloride*, $C_6H_8N_2,AuCl_3$, which crystallises in yellow needles and melts and decomposes at 120°, and a *mercurichloride*, $C_6H_8N_2,2HgCl_2$, which crystallises in needles and melts at 207°. When 4 : 5-dimethylpyrimidine is oxidised with an aqueous solution of potassium permanganate, a *monocarboxylic acid* (probably 5-methylpyrimidine-4-carboxylic acid) is obtained ; this crystallises in compact needles, melts at 190°, forms a *copper* salt which crystallises in rhombs and melts at 259—260°, and when heated above its melting point, yields a *base* (probably 5-methylpyrimidine), which melts at 15° and boils at 142°.

6-*Chloro*-2-*amino*-4 : 5-*dimethylpyrimidine*, obtained by treating iminodimethyluracil with phosphorus oxychloride, crystallises in pointed rods, melts at 215—216°, dissolves in most warm solvents, and forms *picrate*, which crystallises in small yellow plates melting at 198° ; a *hydrochloride*, in lustrous needles ; a *platinichloride*, in yellowish-red needles melting at 250° ; and an *aurichloride*, in long needles, melting at 160°. 2-*Amino*-6-*thio*-4 : 5-*dimethylpyrimidine*, obtained by treating the corresponding chloro-compound with potassium hydrogen sulphide, is a crystalline substance which sinters at 240° and finally melts at 270° ; it forms a crystalline *aurichloride*, *platinichloride*, and *picrate*. 2-*Amino*-6-*anilino*-4 : 5-*dimethylpyrimidine*, obtained by treating the chloro-compound with aniline, crystallises in compact pyramids melting at 202—203°, and forms a crystalline *hydrochloride*, *aurichloride*, and a *dichromate*. The chloro-compound, when reduced with zinc dust and water, yields 2-*amino*-4 : 5-*dimethylpyrimidine*, which separates from aqueous solution in long needles, melts at 214—215°, and forms a *hydrochloride*, which crystallises in pointed needles ; a *platinichloride*, in small, reddish-yellow plates melting and decomposing at 227° ; an *aurichloride*, $C_6H_9N_3,HAuCl_4$, in long, yellow needles melting at 112°, a *gold* salt, $C_6H_9N_3AuCl_3$, as a red, amorphous powder, melting at 142° ; a *ferrocyanide* in yellowish-white plates, and a *picrate* melting at 250°.

The isomeric 2-*chloro*-6-*amino*-4 : 5-*dimethylpyrimidine*, obtained by treating the dichloro-compound with ammonia, crystallises from alcohol in pointed rods, melts at 182—183°, and forms a crystalline *hydrochloride*, *platinichloride*, *dichromate*, and *picrate*. The corresponding 2-*thio*-derivative crystallises in long needles, decomposes above 300°, and forms a crystalline *hydrochloride*, *platinichloride*, and *picrate*. 6-*Amino*-2-*anilino*-4 : 5-*dimethylpyrimidine* crystallises in pointed scales, melts at 166°, forms a crystalline *hydrochloride*, which in aqueous solution gives crystalline precipitates with solutions of auric and platinic chlorides, potassium dichromate, and ferrocyanide, and picric acid. 6-*Amino*-4 : 5 *dimethylpyrimidine* crystallises in compact rods, melts at 230°, forms a *hydrochloride* which crystallises in feathery forms and in aqueous solution gives crystalline precipitates with the solutions just mentioned.

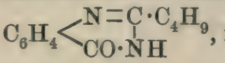
6-*Hydroxy*-4 : 5-*dimethylpyrimidine,* obtained by treating the dichloro-compound with hydriodic acid, crystallises from benzene in rhombic plates, melts at 204°, forms a *hydriodide* (which crystallises in yellow prismatic forms, sinters at 200°, and finally melts at 210°) and a crystalline *aurichloride, platinichloride,* and *picrate.* 6-*Chloro*-4 : 5-*dimethylpyrimidine,* obtained by treating the hydriodide with phosphorus oxychloride, crystallises in small, colourless rods, melts at 51°, boils at 203°, and forms a crystalline *aurichloride, ferrocyanide,* and *picrate,* the corresponding 6-*thio*-derivative crystallises in prismatic forms, softens at 200°, melts at 265°, and forms a crystalline *hydrochloride, aurichloride, platinichloride, dichromate, ferrocyanide,* and *picrate,* and the 6-*anilino*-derivative crystallises in prismatic forms, melts at 152°, and forms a crystalline *hydrochloride, platinichloride, aurichloride, dichromate, ferrocyanide,* and *picrate.*

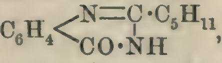
2 : 6-*Diamino*-4 : 5-*dimethylpyrimidine,* obtained by the continued treatment of the 2 : 6-dichloro-compound with ammonia, crystallises in prisms, melts at 192°, and forms a crystalline *hydrochloride* and *platinichloride,* melting at 250°; the corresponding 2 : 6-*dianilino*-derivative crystallises in pointed prisms and melts at 133—134°; and the 2 : 6-*dithio*-derivative crystallises in long rods and decomposes above 300°. 4 : 5-*Dimethyl*-2 : 6-*dimethoxypyrimidine,* obtained by treating the dichloro-compound with sodium and methyl alcohol, crystallises in rhombic needles, melts at 39—40°, boils at 229°, and forms a crystalline *platinichloride, aurichloride,* and *picrate.* R. H. P.

Synthesis of Alkyl Ketodihydroquinazolines from Anthranilic Acid. By AUGUST H. GOTTHELF (*J. Amer. Chem. Soc.*, 1901, **23**, 611—632. Compare Bogert and Gotthelf, Abstr., 1900, i, 412, 608).—When anthranilic acid is heated with propionitrile in a sealed tube, 2-ethyl-4-ketodihydroquinazoline is obtained in a yield amounting to 22½ per cent. of the theoretical; by the addition of propionic anhydride or propionic acid, the yield is increased to about 30 per cent.; some propionylaniline is formed in each case. A mixture of anthranilic acid, acetonitrile, and propionic anhydride furnishes the ethylquinazoline in a yield of 17 per cent.; the corresponding methyl compound is not produced in this reaction. 3-*Methyl*-2-*ethyl*-4-*ketodihydroquinazoline* crystallises in long, colourless needles and melts at 121°. The *hydrochloride* crystallises in needles, and sublimes without melting. The *sulphate* melts at 240—241°, the *picrate* at 191—192°, the *oxalate* at 180—181°, and the *nitrate* and *chromate* melt and decompose at 173—174° and 155° respectively; the *platinichloride* forms a red, crystalline powder.

By the action of butyronitrile on anthranilic acid, 2-propyl-4-ketodihydroquinazoline melting at 199—200° is produced, butyramide also being formed; in presence of butyric anhydride, the yield is increased, whilst with butyric acid the same products are obtained together with some butyrylaniline. When a mixture of anthranilic acid, acetonitrile, and butyric anhydride is heated, the propylquinazoline is produced together with another substance which is probably the corresponding methylquinazoline. 3-*Methyl-2-propyl-4-ketodihydroquinazoline* crystallises in long, colourless needles and melts at 77—78°. The *hydrochloride* forms thin plates and sublimes without melting. The *sulphate* melts at 227—228°, the *picrate* at 183—184°, and the *oxalate* at 193—194°; the *nitrate* melts and decomposes at 159—160°, and the *chromate* gradually darkens above 150°. The *platinichloride* forms coarse, red crystals.

When anthranilic acid, *iso*butyric anhydride, and propionitrile are heated together in a sealed tube, 2-*iso*propyl-4-ketodihydroquinazoline is produced, but no ethylquinazoline is formed. If acetonitrile is used instead of propionitrile, the same quinazoline is obtained but in smaller yields; it melts at 231—232°, and probably exists in two forms. 3-*Methyl*-2-iso*propyl-4-ketodihydroquinazoline* crystallises in long, silky needles and melts at 78—79°. The *hydrochloride* forms rectangular plates; the *sulphate* decomposes on heating, the *picrate* melts at 213—214°; and the *platinichloride* is obtained in coarse, red crystals.

By the action of *iso*valeronitrile on anthranilic acid, 2-iso*butyl-4-ketodihydroquinazoline*,  $C_6H_4<\begin{matrix}N=C\cdot C_4H_9\\ \mid \\ CO\cdot NH\end{matrix}$, is produced in a yield of 5 per cent.; in the presence of *iso*valeric anhydride, the yield is increased to 35 per cent., *iso*valerylaniline and *iso*valeramide being simultaneously formed. It crystallises in small needles, melts at 194—195°, and is readily soluble in alcohol or hot benzene, fairly so in ether or hot water, and very slightly so in cold water. The 3-*methyl*-2-iso*butyl-4-ketodihydroquinazoline* forms colourless needles and melts at 68—69°; the *hydrochloride* crystallises in needles; the *sulphate* melts at 228—229°; the *picrate* at 192°, and the *oxalate* at 204—205°; the *nitrate* and *chromate* decompose at 171—172° and 154° respectively. The *platinichloride* forms coarse, brown needles.

When anthranilic acid is heated with *iso*hexonitrile, 2-iso*amyl-4-ketodihydroquinazoline*,  $C_6H_4<\begin{matrix}N=C\cdot C_5H_{11}\\ \mid \\ CO\cdot NH\end{matrix}$, is obtained in a yield of 18 per cent.; in the presence of *iso*hexoic acid, the yield is increased to 37 per cent., and *iso*hexoylaniline and *iso*hexoamide are simultaneously produced; it crystallises in needles, melts at 184°, and is soluble in ether, alcohol, benzene, or hot water. 3-*Methyl*-2-iso*amyl-4 ketodihydroquinazoline* crystallises in small needles and melts at 40—41°. The *hydrochloride* forms fine needles, the *nitrate* decomposes at 160—161°, and the *picrate* melts at 164—165°,

The action of a nitrile on anthranilic acid in presence of the anhydride of a lower acid was investigated, with the following results. Propionitrile and acetic anhydride yield the methylquinazoline. *iso*-Hexonitrile and *iso*butyric anhydride furnish the *iso*propylquinazoline with probably some *iso*amylquinazoline. With *iso*hexonitrile and butyric anhydride, the propylquinazoline is obtained together with another substance which is probably the *iso*amyl compound.

The action of a nitrile on anthranilic acid in presence of a higher acid was also examined. Acetonitrile and propionic acid yield a mixture which probably consists of the methyl- and ethyl-quinazolines; butyronitrile and decoic acid furnish the propylquinazoline, and with *iso*hexonitrile and decoic acid the *iso*amylquinazoline is produced.

The action of a nitrile on anthranilic acid in presence of a lower acid gave the following results. Acetonitrile and formic acid yield formylanthranilic acid but no quinazoline; a similar result was obtained with propionitrile and formic acid. *iso*Hexonitrile and formic acid furnish a small quantity of the *iso*amylquinazoline, together with *iso*hexoamide and a substance which is probably 4-ketodihydroquinazoline. *iso*Hexonitrile and propionic acid yield the *iso*amylquinazoline.

When anthranilic acid is heated with butyric or *iso*hexoic acid, no action takes place, whilst with butyric or *iso*valeric anhydride the corresponding acylanthranilic acids are obtained. iso*Valerylanthranilic acid* crystallises from water in needles and melts at 110—111°.

E. G.

4:4′-Diaminodiphenylamine-3′-sulphonic Acid. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 119009).—4:4′-*Diaminodiphenylamine-3′-sulphonic acid*, prepared from 4:4′-diaminodiphenylamine-2:3′-disulphonic acid by boiling the latter with 50 per cent. sulphuric acid, separates from the cooled solution in the form of the sulphate; the free acid forms silvery greyish-blue crystals sparingly soluble in water.

The disulphonic acid employed in this reaction is obtained by condensing chloro-*p*-nitrobenzene-*o*-sulphonic acid with *p*-phenylenediaminesulphonic acid and reducing the resulting nitroamine.

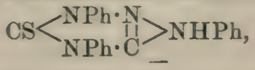
G. T. M.

Carbodiphenylimide. By CARL SCHALL (*J. pr. Chem.*, 1901, [ii], **64**, 261—273. Compare Abstr., 1900, i, 464).—On melting a mixture of carbodiphenylimide and benzoic acid, a *monobenzoyldiphenylcarbamide*, NHPh·CO·NBzPh, is formed; it crystallises in long needles melting at 129°, decomposes into phenylcarbimide and benzanilide on heating, and is probably identical with the compound obtained by Dains (Abstr., 1899, i, 593) from ethyl phenyliminophenylcarbamate and benzoyl chloride.

Carbodiphenylimide can be obtained in a colloidal (γ) form by treating the ordinary form (α) with insufficient benzene to dissolve it. The γ-form is of gelatinous consistency and is reconverted into the ordinary variety by treatment with acetic acid.

On removing sulphur from phenyl*cyclo*hexylthiocarbamide by mercuric oxide in the presence of boiling chloroform, an oil is obtained which is probably a reduced carbodiphenylimide; on dissolving the oil in acetic acid, phenyl*cyclo*hexylcarbamide (m. p. 180°) separates. From di-α-tetrahydronaphthylthiocarbamide by treatment with α-naphthylamine and lead oxide in alcoholic solution, a derivative of a hydrated carbodi-α-naphthylimide, *α-naphthyldi-α-tetrahydronaphthylguanidine*, $C_{10}H_7·N\vdots C(NH·C_{10}H_{11})_2$, is obtained; it crystallises in short, microscopic prisms melting at 177—179°.

The author has obtained the triphenylthiotriazolone (m. p. 180°), which is formed from Wessel's dicarbo-base (*loc. cit.*) and carbon disulphide, by the interaction of anilinodiphenylguanidine and ethyl trithiocarbonate, a fact which confirms the formula,



$$CS\left\langle\begin{matrix}NPh\cdot N\\ \quad\ \ \| \\ NPh\cdot C\end{matrix}\right\rangle NHPh,$$

for the thiotriazolone. K. J. P. O.

The Fourteenth Isomeride of Rosinduline. By Friedrich Kehrmann and Emil Ott (*Ber.*, 1901, **34**, 3092—3098).—4-Amino-1 : 2-naphthaquinone condenses with 2 : 3′- and 2 : 4′-diaminodiphenylamines, forming amino*iso*rosindulines, from which, by treatment with nitrous acid, the fourteenth and fifteenth isomerides of rosinduline (*iso*rosindulines) are obtained.

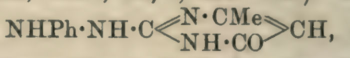
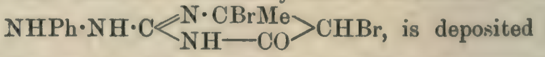
The *dihydrochloride* of 2 : 4′-diaminodiphenylamine crystallises in long, colourless prisms and condenses with 4-amino-1 : 2-naphthaquinone, forming 5 : 4′-*diaminophenyl-αβ-naphthaphenazonium chloride* ; when treated with acetic anhydride, this yields 4′-*acetylaminorosinduline* and 5 : 4′-*diacetylaminorosinduline.* The *chloride* of the monoacetyl compound crystallises in red laminæ with a bronze-like lustre and the *dichromate* is an insoluble, scarlet, crystalline powder. The *chloride* of the diacetyl compound forms orange-yellow, leaf-like crystals with a golden-green iridescence, and the *dichromate* is a red, crystalline powder. The chloride of the monoacetyl compound, when treated with nitrous acid, yields *acetyl*iso*rosinduline chloride*, which is isolated by means of the additive *compound* with ferric chloride, forms golden-yellow, leaf-like crystals, and is easily converted into the *dichromate*, which is an insoluble, red powder ; this acetyl compound, when treated with sulphuric acid and the resulting solution precipitated with sodium bromide, yields iso*rosinduline* (No. 14) (4′-*aminophenylnaphthaphenazonium bromide*), which is obtained as a reddish-brown, crystalline powder. R. H. P.

The Fifteenth Isomeride of Rosinduline. By Friedrich Kehrmann and Paul Nüesch (*Ber.*, 1901, **34**, 3099—3104).—5 : 3′-*Diaminophenyl-αβ-naphthaphenazonium chloride*, obtained by the condensation of 4-amino-1 : 2-naphthaquinone with the hydrochloride of diaminodiphenylamine, crystallises in aggregates of dark-red needles and was only obtained pure by the hydrolysis of the *diacetyl* derivative, which forms a *chloride* (small, scarlet-red needles with a metallic lustre) and a *dichromate* (red, crystalline precipitate). The *monoacetyl* (3′-*acetylamino*-) derivative, obtained when the diamino-chloride reacts with acetic anhydride at the ordinary temperature, forms a *chloride* which shows a yellow and red fluorescence in alcoholic solution and crystallises in green, iridescent aggregates, and a *dichromate*, which was obtained as a deep-red, crystalline precipitate.

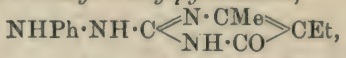
*Acetyl*iso*rosinduline* (3′-*acetylaminophenyl-αβ-naphthaphenazonium chloride*), obtained when the chloride of the monoacetyl compound is treated with nitrous acid, is best purified by conversion into the *bromide*, which when hydrolysed with sulphuric acid yields the bromide of 3′-*aminophenylnaphthaphenazonium* (iso*rosinduline* No. 15), which is obtained as dark reddish-yellow crystals with a green, metallic lustre ; the *dichromate* of the *iso*rosinduline crystallises from water in lustrous golden-yellow laminæ.

The paper concludes with a comparison of the absorption spectra of the salts of phenylnaphthaphenazonium and the fourteenth and fifteenth isomerides of *iso*rosinduline. R. H. P.

Preparation of Hydroxytriazoles and their Sulphonic Acids. K. OEHLER (D.R.-P. 119901).—Hydroxytriazoles can be prepared either by fusing the sulphonic acids of the triazoles with sodium hydroxide or by heating the compounds under pressure with a concentrated solution of the alkali. G. T. M.

Isomeric Anilinoguanidines. By GUIDO PELLIZZARI and CESARE RONCAGLIOLO (*Gazzetta*, 1901, **31**, i, 513—526).—2-*Phenylhydrazine*-4-*methylpyrimidone*,  $\mathrm{NHPh\cdot NH\cdot C}\left<\begin{matrix}\mathrm{N\cdot CMe}\\ \mathrm{NH\cdot CO}\end{matrix}\right>\mathrm{CH}$, obtained by the condensation of anilinoguanidine and ethyl acetoacetate with elimination of water and alcohol, crystallises from alcohol in minute, white needles which have no definite melting point, but begin to redden at about 200° and decompose at about 230°; it is slightly soluble in water and exhibits both basic and acid functions. When heated under pressure with moderately concentrated hydrochloric acid, it is completely converted into phenylhydrazine and methyluracyl, a reaction which gives its constitution. Its *hydrochloride*, $C_{11}H_{12}ON_4,2HCl$, separates in white needles, which redden at 200°, melt and decompose at 220—230° and are moderately soluble in alcohol or water. Its *dibromide*,  $\mathrm{NHPh\cdot NH\cdot C}\left<\begin{matrix}\mathrm{N\cdot CBrMe}\\ \mathrm{NH—CO}\end{matrix}\right>\mathrm{CHBr}$, is deposited from acetic acid solution as a white, crystalline powder decomposing at 220—222°; it dissolves in dilute potassium hydroxide but is insoluble in dilute acids.

2-*Phenylhydrazine*-4-*methyl*-5-*ethylpyrimidone*,



$$\mathrm{NHPh\cdot NH\cdot C}\left<\begin{matrix}\mathrm{N\cdot CMe}\\ \mathrm{NH\cdot CO}\end{matrix}\right>\mathrm{CEt},$$

prepared from anilinoguanidine and ethyl ethylacetoacetate, crystallises from alcohol in spherical aggregates of slender needles, which soften at 215° and melt at about 235°.

2-*Phenylmethylhydrazine*-4-*methylpyrimidone*, $C_{12}H_{14}ON_4$, prepared from anilinomethylguanidine and ethyl acetoacetate, crystallises from dilute alcohol in long, white needles melting at 192°; it is soluble in benzene or dilute acids or alkalis and gives a crystalline picrate and platinichloride.

Aminophenylguanidine shows a behaviour quite different from that of its isomeride, as it contains a hydrazine group, by virtue of which it is able to form condensation products with aldehydes and ketones.

Ethylideneaminophenylguanidine nitrate,

$$CHMe\!:\!N\cdot NPh\cdot C(NH_2)\!:\!NH,HNO_3,$$

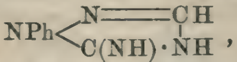
obtained by the action of acetaldehyde on aminophenylguanidine nitrate, separates in small, white needles melting at 182°; it is soluble in water or alcohol and when boiled in acid solution is resolved into its components.

Chloralaminophenylguanidine nitrate,

$$CCl_3\cdot CH(OH)\cdot NH\cdot NPh\cdot C(NH_2)\!:\!NH,HNO_3,$$

prepared from chloral and aminophenylguanidine nitrate, is deposited from aqueous solution in slender, acicular crystals which melt at 130 and are soluble in alcohol.

The *ethyl acetoacetate* derivative of *aminophenylguanidine nitrate*, $CO_2Et\cdot CH_2\cdot CMe{:}N\cdot NPh\cdot C(NH_2){:}NH,HNO_3$, separates from water in short crystals melting at 160°. 5-*Imino*-1-*phenyltriazoline*,



$$\mathrm{NPh}{<}\begin{array}{l}\mathrm{N{=\!=\!=}CH}\\ \qquad\quad |\\ \mathrm{C(NH)\cdot NH}\end{array},$$

obtained by the action of formic acid on aminophenylguanidine, separates in long, shining, white needles melting at 157°; it has basic properties, forming well-defined salts, and is very soluble in alcohol and to a less extent in water or benzene. The *picrate*, $C_8H_8N_4,C_6H_3O_7N_3$, crystallises from water in silky, yellow needles melting at 175°, whilst the *platinichloride*, $(C_8H_8N_4)_2,H_2PtCl_6$, melts at 197°. T. H. P.

Compounds of Aminophenylguanidine with Aldehydes and Ketones. By GUIDO PELLIZZARI and R. RICKARDS (*Gazzetta*, 1901, 31, i, 526—536).—The possibility of employing aminophenylguanidine as a reagent for the characterisation of aldehydes and ketones has been studied by the authors. With all the aldehydes tried, characteristic compounds were obtained, but this was only the case with a few of the ketones to which the test was applied. The aminophenylguanidine was employed in the form of nitrate, the condensation products obtained being described below.

Furfurylideneaminophenylguanidine nitrate,

$$C_4OH_3\cdot CH{:}N\cdot NPh\cdot C(NH_2){:}NH,HNO_3,$$

crystallises from alcohol in transparent, colourless prisms which melt and decompose at 171° and dissolve in water and to a less extent in chloroform, benzene, or ether. The corresponding *picrate*,

$$C_{12}H_{12}ON_4,C_6H_3O_7N_3,$$

crystallises from alcohol in needles which melt and decompose at 218°. The *platinichloride*, $(C_{12}H_{12}ON_4)_2H_2PtCl_6$, separates in small, orange-yellow crystals melting and decomposing at 207°.

o-*Hydroxybenzylideneaminophenylguanidine nitrate*,

$$OH\cdot C_6H_4\cdot CH{:}N\cdot NPh\cdot C(NH_2){:}NH,HNO_3,$$

crystallises from alcohol in shining plates which melt and decompose at 207—208° and are moderately soluble in water; under the influence of light, it becomes reddish-yellow. The *picrate*, $C_{14}H_{14}ON_4,C_6H_3O_7N_3$, separates from alcohol in slender, yellow needles which melt and decompose at 254° and are moderately soluble in water. The *platinichloride*, $(C_{14}H_{14}ON_4)_2,H_2PtCl_6$, forms orange-yellow needles melting at 220—221° and is slightly soluble in water or alcohol.

m-Nitrobenzylideneaminophenylguanidine nitrate,

$$NO_2\cdot C_6H_4\cdot CH{:}N\cdot NPh\cdot C(NH_2){:}NH,HNO_3,$$

crystallises from alcohol in small, white needles which melt and decompose at 199° and are readily soluble in water. The corresponding *picrate* separates from alcohol in golden-yellow needles melting and decomposing at 250° and dissolving slightly in water.

Vanillideneaminophenylguanidine picrate,

$$OMe\cdot C_6H_3(OH)\cdot CH{:}N\cdot NPh\cdot C(NH_2){:}NH,C_6H_3O_7N_3,$$

crystallises from alcohol in needles which melt and decompose at 234° and are slightly soluble in water.

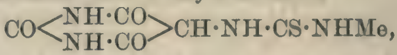
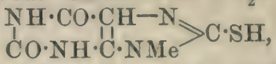
Citrylideneaminophenylguanidine [*citralaminophenylguanidine*] *nitrate*, $CMe_2{\cdot}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH{:}N{\cdot}NPh{\cdot}C(NH_2){:}NH,HNO_3$, separates from dilute alcohol in white crystals which soften at 110° and melt completely at about 120°; it is very soluble in alcohol, benzene, or chloroform and to a less extent in water. The *picrate* crystallises from alcohol in shining, yellow scales melting and decomposing at 166—170° and dissolving slightly in water. The fact that these compounds have indefinite melting points is possibly due to their existence in two isomeric modifications, similar to those obtained by Tiemann in the case of the semicarbazones.

Methylbenzylideneaminophenylguanidine [*acetophenoneaminophenylguanidine*] *nitrate*, $CMePh{:}N{\cdot}NPh{\cdot}C(NH_2){:}NH,HNO_3$, is deposited from alcohol in shining, flattened crystals melting and decomposing at 181° and is slightly soluble in alcohol. The *picrate* separates from alcohol in yellow crystals which melt and decompose at 220—221°.

With glyoxal, aminophenylguanidine gives a crystalline compound which was not further investigated; with dextrose, lactose, benzophenone, &c., no condensation products could be obtained.

T. H. P.

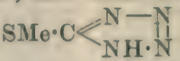
3-Alkylxanthine Derivatives. C. F. BOEHRINGER & SONS (D.R.-P. 120437).—Uramil, when condensed with alkyl and aryl thiocarbimides, yields alkylthio-ψ-uric acids; these compounds, when heated with hydrochloric acid, give rise to 3-alkylthiouric acids, which by the action of nitrous acid are transformed into 3-alkylxanthines.

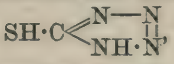
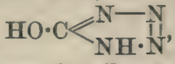
Methylthio-ψ-uric acid,  $CO<\begin{matrix}NH{\cdot}CO\\NH{\cdot}CO\end{matrix}>CH{\cdot}NH{\cdot}CS{\cdot}NHMe$, produced from uramil and methyl thiocarbimide in the presence of potassium hydroxide, crystallises in lustrous leaflets with $1H_2O$ and melts at 110°. 3-*Methylthiouric acid*,  $\begin{matrix}NH{\cdot}CO{\cdot}CH{-}N\\ | \quad\quad \| \\ CO{\cdot}NH{\cdot}C{\cdot}NMe\end{matrix}{>}C{\cdot}SH$, obtained by heating it with 5 per cent hydrochloric acid, is slightly soluble in water or alcohol and yields an amorphous silver salt. 3-*Methylxanthine* is formed from the latter acid by the action of sodium nitrite and hydrochloric acid; it crystallises from water in needles melting at 384°.

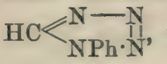
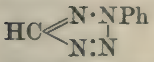
3-*Phenylthio-ψ-uric acid*, a crystalline compound sparingly soluble in alcohol or water, yields successively 3-*phenylthiouric acid* and 3-*phenylxanthine*, the latter compound crystallising in lustrous leaflets and melting at 337°.

3-*Ethylxanthine* crystallises in lamellæ, and 3-*benzylxanthine* in four-sided plates; these bases melt respectively at 360° and 342°.

G. T. M.

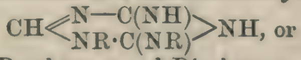
Tetrazole. By MARTIN FREUND and TH. PARADIES (*Ber.*, 1901, **34**, 3110—3122).—*Methylthiosemicarbazide hydriodide*, prepared by treating thiosemicarbazide with methyl iodide, is a crystalline soluble salt which sinters at 136°, melts at 140°, and when treated with nitrous acid yields *methylmercaptotetrazole*,  $SMe{\cdot}C<\begin{matrix}N{-}N\\NH{\cdot}N\end{matrix}$; this crystallises in rhombic prisms, sinters at 144°, melts and decomposes at 151°, forms characteristic *silver* and *copper* salts and, when oxidised with potassium permanganate, yields the corresponding *sulphone*, which crystallises like ice flowers, sinters at 110°, melts at 120°, and forms characteristic *potassium* and *silver* salts.

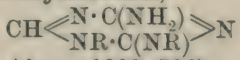
Tetrazolethiol,  $\mathrm{SH{\cdot}C}\left\langle\begin{matrix}\mathrm{N{-}N}\\ \mathrm{NH{\cdot}N}\end{matrix}\right.$, obtained by the action of hydriodic acid on methylmercaptotetrazole, crystallises in white needles melting and decomposing at 205°, forms a *sodium* salt crystallising with $1\frac{1}{2}H_2O$, and when treated with dilute nitric acid, yields tetrazole. *Tetrazolesulphonic acid,* obtained by oxidising the thiol with nitric acid, is a syrup; it forms definite *silver, lead,* and *barium* salts, and when fused with potassium hydroxide yields *tetrazolol,*  $\mathrm{HO{\cdot}C}\left\langle\begin{matrix}\mathrm{N{-}N}\\ \mathrm{NH{\cdot}N}\end{matrix}\right.$, which crystallises from water, melts at 254°, and forms the *silver* salt, $CN_4Ag{\cdot}OAg$.

Phenylmercaptotetrazole (from 4-phenylthiosemicarbazide and nitrous acid), when oxidised with chromic acid, yields the *phenyltetrazole,*  $\mathrm{HC}\left\langle\begin{matrix}\mathrm{N{-}N}\\ \mathrm{NPh{\cdot}N}\end{matrix}\right.$, which melts at 65—66°, the isomeride  $\mathrm{HC}\left\langle\begin{matrix}\mathrm{N{\cdot}NPh}\\ \mathrm{N{:}N}\end{matrix}\right.$ being an oil (see Abstr., 1894, i, 53); this phenyltetrazole forms a *mononitro*-derivative which melts and decomposes at 205°, and when reduced yields the corresponding *amino*-compound which crystallises in silky needles, melts at 155°, and when oxidised yields tetrazole.

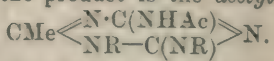
These researches support the view that tetrazole is a tautomeric substance, the tautomerism being destroyed by the substitution of the hydrogen atom by a phenyl group. R. H. P.

α-Disubstituted Biguanides and Guanamines. By W. CRAMER (*Ber.*, 1901, **34**, 2594—2603).—An alcoholic solution of guanidine, $NH_2{\cdot}C(NH){\cdot}NH_2$, is obtained readily by mixing equivalent amounts of guanidine hydrochloride and sodium ethoxide in alcoholic solution, and filtering from the precipitated sodium chloride. When this is mixed with an alcoholic solution of a disubstituted thiocarbamide, $CS(NHR)_2$, and the whole heated with precipitated mercuric oxide, and filtered from the mercuric sulphide formed, an α-disubstituted (compare Emich, Abstr., 1891, 1180) *biguanide*, $NH_2{\cdot}C(NH){\cdot}NH{\cdot}C(NR){\cdot}NHR$, or $C(NH_2)_2{:}N{\cdot}C(NR){\cdot}NHR$, a monoacid base with basic properties, crystallises from the filtrate as it cools. If this is digested at 100° with benzoic anhydride in alcoholic solution, it is converted into a *dibenzoyl* derivative. If it is boiled with excess of anhydrous formic acid, it condenses to a disubstituted *formoguanamine*,





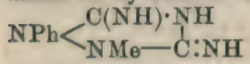
$$\mathrm{CH}\left\langle\begin{matrix}\mathrm{N{-}C(NH)}\\ \mathrm{NR{\cdot}C(NR)}\end{matrix}\right\rangle\mathrm{NH},\ \text{or}\ \mathrm{CH}\left\langle\begin{matrix}\mathrm{N{\cdot}C(NH_2)}\\ \mathrm{NR{\cdot}C(NR)}\end{matrix}\right\rangle\mathrm{N}$$

(compare Bamberger and Dieckmann, Abstr., 1892, 736), a monoacid base which can be precipitated from solution by ammonia. If acetic anhydride is used instead of formic acid, the product is the *acetyl* derivative of a disubstituted *acetoguanamine*,  $\mathrm{CMe}\left\langle\begin{matrix}\mathrm{N{\cdot}C(NHAc)}\\ \mathrm{NR{-}C(NR)}\end{matrix}\right\rangle\mathrm{N}$.

The following substances were prepared; the numbers are melting points:—*Diphenyl* derivatives (R = Ph): *biguanide*, 167°; *hydrochloride*, 234—235°; *platinichloride*, nitrate, 216° (not 321°, Bamberger, Abstr., 1881, 43); *dibenzoyl* derivative, yellow, 162°. *Formoguanamine*, yellowish, 206°; *platinichloride*, yellow. *Acetylacetoguanamine*, yellowish, 217°.—*Di-*o*-tolyl* derivatives (R = C_6H_4Me): *biguanide*, 178°; *hydrochloride*, 245°. *Formoguanamine*, 255°. *Acetylacetoguanamine*, 191°. —*Di-*p*-tolyl* derivatives (R = C_6H_4Me): *biguanide*, 140°, crystallised with 1EtOH, 90°; *nitrate*, 218°. *Formoguanamine*, 222°.—*Di-*1 : 2 : 4-*xylyl* derivatives (R = $C_6H_3Me_2$, the *dithiocarbamide* melts at 152°): *biguanide*, oily; hydrochloride, crystalline; nitrate, 203°.

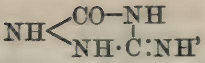
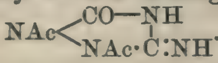
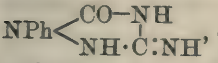
Several disubstituted biguanides with different substituting groups were also prepared. *a-Phenylethylbiguanide* melts at 131—132°. By treating guanylphenylthiocarbamide with silver nitrate in the presence of 1 : 2 : 4-xylidine or *o*-anisidine, there were obtained respectively 1 : 2 : 4-*xylylphenylbiguanide*, pasty; *nitrate*, 204°; and o-*anisylphenylbiguanide*, pasty; *nitrate*, 206°. C. F. B.

Researches on Guanazole. By GUIDO PELLIZZARI and CESARE RONCAGLIOLO (*Gazzetta*, 1901, **31**, i, 477—513. Compare Abstr., 1892, 356, and 1894, i, 517).—The following derivatives of phenylguanazole (*loc. cit.*) have been prepared:—*Acetylphenylguanazole*, $C_{10}H_{11}ON_5$, crystallises from water in elongated, flat prisms containing $1H_2O$ and melts at 244°; it is moderately soluble in alcohol, is hydrolysed readily by bases or acids, and loses its water of crystallisation in the air, the crystals becoming opaque. *Diacetylphenylguanazole*, $C_{12}H_{13}O_2N_5$, separates from alcohol in small, white crystals, from water in transparent, white prisms melting at 212°, and from very dilute acetic acid in silky needles containing $4H_2O$; on boiling with dilute hydrochloric acid, it loses acetic acid, yielding phenylguanazole hydrochloride. *Tetra-acetylphenylguanazole*, $C_{16}H_{17}O_4N_5$, obtained by boiling the diacetyl compound in a reflux apparatus with acetic anhydride, separates on the addition of a little alcohol in small needles which melt at 157° and when crystallised from water lose two acetyl residues, giving the preceding compound. Phenylguanazole hence contains 4 replaceable hydrogen atoms. *Benzylidenephenylguanazole*, $C_{15}H_{13}N_5$, obtained by the action of benzaldehyde on phenylguanazole, separates from alcohol in crystals melting at 228° and is slightly soluble in ether, benzene, or chloroform; dilute mineral acids decompose it in the cold, giving benzaldehyde and the corresponding salt of phenylguanazole. *Nitrosophenylguanazole*, $C_8H_8ON_6$, is an orange-yellow, unstable powder which melts at 247° and with sulphuric acid and phenol gives Liebermann's reaction. With methyl iodide, phenylguanazole gives the hydriodide of the phenylmethylguanazole which has been already obtained (*loc. cit.*) by the action of dicyanodiamide on hydrazomethylphenyl hydrochloride and has the constitution

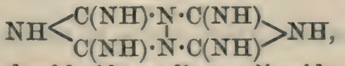


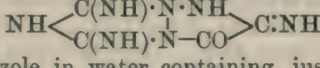
$$\mathrm{NPh}\Big\langle\begin{array}{l}\mathrm{C(NH)\cdot NH}\\ \qquad\qquad\ |\\ \mathrm{NMe{-}C{:}NH}\end{array}$$

; this fact tends to confirm the iminic formula for phenylguanazole. Phenylguanazole platinichloride (*loc. cit.*) does not lose hydrogen chloride when boiled with water, a fact explained by the absence in the nucleus of double bonds.

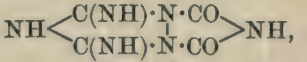
Iminourazole,  $\mathrm{NH}<\begin{matrix}\mathrm{CO{-}NH}\\ \mid\\ \mathrm{NH\cdot C{:}NH}\end{matrix}$, which represents an intermediate compound between urazole and guanazole, is obtained either by the interaction of dicyanodiamidine hydrochloride on hydrazine monohydrochloride or by the action of carbamide on aminoguanidine hydrochloride. It separates from very dilute acetic acid in small, white, acicular crystals melting at 285°, shows slight acid and basic properties, reduces ammoniacal silver nitrate, and gives a red coloration with ferric chloride. *Diacetyliminourazole*, $C_6H_8O_3N_4$, crystallises from alcohol in small, silky needles melting at above 300°; its probable constitution is  $\mathrm{NAc}<\begin{matrix}\mathrm{CO{-}NH}\\ \mid\\ \mathrm{NAc\cdot C{:}NH}\end{matrix}$. *Phenyliminourazole*,  $\mathrm{NPh}<\begin{matrix}\mathrm{CO{-}NH}\\ \mid\\ \mathrm{NH\cdot C{:}NH}\end{matrix}$, obtained (1) by the action of carbamide on phenylaminoguanidine hydrochloride, (2) by the interaction of dicyanodiamidine and phenylhydrazine, or (3) by heating phenylguanazole with potassium hydroxide solution in an autoclave, separates from water in small, shining, acicular crystals melting at 272°; it exhibits faint acid and basic properties, and forms a crystalline *silver* salt, $C_8H_7ON_4Ag$, and a *hydrochloride*, $C_8H_8ON_4,HCl + H_2O$, separating in white, acicular crystals.

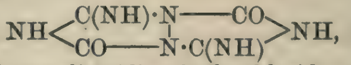
Guanazole may be regarded as a symmetrical secondary hydrazine and as such it is capable of condensing with dicyanodiamide, forming a compound, guanazoguanazole, containing two guanazole rings in the molecule. The replacement of one or more of the four imino-groups in guanazoguanazole by oxygen atoms leads to the production of other condensed molecules; such of these compounds as have been prepared are described below.

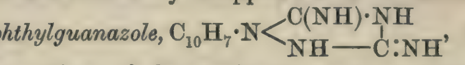
Guanazoguanazole,  $\mathrm{NH}<\begin{matrix}\mathrm{C(NH)\cdot N\cdot C(NH)}\\ \mid\\ \mathrm{C(NH)\cdot N\cdot C(NH)}\end{matrix}>\mathrm{NH}$, obtained by the action of guanazole hydrochloride on dicyanodiamide, or, better, by the interaction of 2 mols. of dicyanodiamide and 1 mol. of a hydrazine salt, crystallises from alcohol in small, shining plates, which, when heated on platinum, do not melt but gradually disappear without carbonising; when heated in a glass tube, it sublimes in the form of small, acicular crystals; it is slightly soluble in water and shows distinct basic functions. The hydrochloride is unstable; the *platinichloride*, with $2H_2O$, forms small, orange prisms; the *picrate*, $C_4H_6N_8,C_6H_3O_7N_3$, separates from water in spheroidal aggregates of crystals which melt and decompose at above 270° and are slightly soluble in alcohol; with silver nitrate, it forms a *double* compound, $C_4H_6N_8,AgNO_3$, obtained as a white precipitate. The *diacetyl* derivative, $C_4H_4N_8Ac_2$, and the *triacetyl* derivative, $C_4H_3N_8Ac_3$, obtained as a white powder, are insoluble in water and melt and decompose at a high temperature.

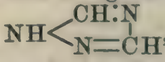
Iminourazoguanazole,  $\mathrm{NH}<\begin{matrix}\mathrm{C(NH)\cdot N\cdot NH}\\ \mid\\ \mathrm{C(NH)\cdot N{-}CO}\end{matrix}>\mathrm{C{:}NH}$, obtained by dissolving guanazoguanazole in water containing just the requisite quantity of hydrochloric acid, and boiling the solution in a reflux apparatus until a small portion completely dissolves in potassium hydroxide solution, forms a white, crystalline powder insoluble in water.

It shows faintly basic properties, yielding with concentrated hydrochloric acid spheroidal crystalline aggregates of a hydrochloride which is decomposed by water or even in the air; it gives no picrate or platinichloride. Its acid properties are more marked, as it dissolves readily in potassium hydroxide solution, from which it is precipitated by acids.

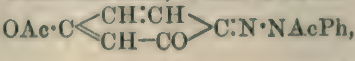
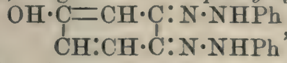
Urazoguanazole,  $\mathrm{NH}{<}\begin{matrix}\mathrm{C(NH)\cdot N\cdot CO}\\ \mathrm{C(NH)\cdot N\cdot CO}\end{matrix}{>}\mathrm{NH}$, prepared by the interaction of molecular proportions of urazole and dicyanodiamide, or of guanazole and biuret, forms a white powder which is insoluble in water or alcohol and when heated in a small tube sublimes and partially decomposes with evolution of ammonia. In this compound, the basic properties have entirely disappeared, but the acid properties have become more marked.

Iminourazoiminourazole,  $\mathrm{NH}{<}\begin{matrix}\mathrm{C(NH)\cdot N\text{——}CO}\\ \mathrm{CO\text{——}N\cdot C(NH)}\end{matrix}{>}\mathrm{NH}$, obtained by the action of excess of dicyanodiamidine hydrochloride on hydrazine hydrochloride, separates from aqueous acetic acid as a white, indistinctly crystalline, infusible powder, which when heated on platinum does not melt but slowly disappears with formation of fumes.

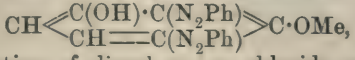
a-Naphthylguanazole,  $\mathrm{C_{10}H_7\cdot N}{<}\begin{matrix}\mathrm{C(NH)\cdot NH}\\ \mathrm{NH\text{——}C{:}NH}\end{matrix}$, prepared from molecular proportions of dicyanodiamide and α-naphthylhydrazine hydrochloride, is deposited from aqueous solution in white, acicular crystals melting at 230°; it has well-defined basic properties, forming well crystallised salts with acids. Its *hydrochloride* crystallises from alcohol in white prisms, which melt at 273° and dissolve readily in water. It gives a flocculent, yellow platinichloride and a well crystallised picrate.

The authors propose a new method of nomenclature for guanazole and similar compounds, taking 1 : 2 : 4-triazole,  $\mathrm{NH}{<}\begin{matrix}\mathrm{CH{:}N}\\ \mathrm{N{=}CH}\end{matrix}$, as the fundamental nucleus. The names of the compounds described in this paper would then become: guanazole, 3 : 5-di-iminotriazolidine; phenylguanazole and the other mono-substituted guanazoles, 1-phenyl-3 : 5-di-iminotriazolidine; phenylmethylguanazole, 1-phenyl-2 methyl-3 : 5-di-iminotriazolidine; iminourazole, 3 : 5-iminotriazolidone; phenyliminourazole, 1-phenyl-3-imino-5-triazolidone; guanazoguanazole, 3 : 5-di-iminotriazolidinyl-3 : 5-di-iminotriazolidine; iminourazoguanazole, 3 : 5-iminotriazolidone; urazoguanazole, 3 : 5-triazolidonyl-3 : 5-diiminotriazolidine; iminourazoiminourazole, 3 : 5-iminotriazolidonyl-3 : 5-iminotriazolidone.

T. H. P.

Two Modifications of Benzene-4-azoresorcinol and the Constitution of the Hydroxyazo-compounds. By William R. Orndorff and E. D. Thebaud (*Amer. Chem. J.*, 1901, 26, 159—166. Compare Will and Pukall, Abstr., 1887, 660, and Goldschmidt and Pollak, Abstr., 1892, 974).—Diacetylbenzene-4-azoresorcinol, which is formulated by Goldschmidt and Pollak as  $\mathrm{OAc\cdot C}{<}\begin{matrix}\mathrm{CH{:}CH}\\ \mathrm{CH{-}CO}\end{matrix}{>}\mathrm{C{:}N\cdot NAcPh}$, reacts with phenylhydrazine to form a *phenylhydrazone* which crystallises from benzene in deep-red granules and melts at 163°; when hydrolysed, it gives the *bisphenylhydrazone* of 4-hydroxy-1:2-benzoquinone,  $\begin{array}{l} OH\cdot C{=}CH\cdot C{:}N\cdot NHPh \\ CH{:}CH\cdot C{:}N\cdot NHPh \end{array}$, which crystallises from dilute acetic acid in dark red needles and melts sharply at 160°.

The *monomethyl ether* of 2:4-bisbenzeneazoresorcinol,



$$CH\left<\begin{array}{l} C(OH)\cdot C(N_2Ph) \\ CH{=}C(N_2Ph) \end{array}\right>C\cdot OMe,$$

prepared by the action of diazobenzene chloride on resorcinol monomethyl ether, crystallises from a mixture of chloroform and alcohol in short, red needles and melts at 189—190°.

Benzeneazoresorcinol monomethyl ether was found to melt at 123°; Will (Abstr., 1888, 457) gives 114° as the melting point. T. M. L.

Sulphonated Hydroxyazo-colouring Matters and their Salts.

By Paul Sisley (*Bull. Soc. Chim.*, 1901, [iii], **25**, 862—877).—Orange-II, $SO_3Na\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot OH$, is a very stable substance, the sodium being eliminated only by boiling with a large excess of concentrated hydrochloric acid. The product thus obtained crystallises in reddish-brown needles and is a powerful acid, readily decomposing sodium chloride or sulphate with the precipitation of Orange-II. Chrysoin, $SO_3Na\cdot C_6H_4\cdot N_2\cdot C_6H_3(OH)_2$, is more easily decomposed than Orange-II; the free acid forms small, steel-grey crystals and also has the power of decomposing metallic salts. Crystal-Ponceau, or Ponceau-6R, $C_{10}H_7\cdot N_2\cdot C_{10}H_4(SO_3Na)_2\cdot OH$, is only decomposed by heating with concentrated sulphuric acid; the free acid thus obtained forms small, red crystals and decomposes sodium hydrogen sulphate or phosphate in the cold. The powerful acid properties of these colouring matters afford a means of preparing a number of metallic salts, which are described in detail in the paper. N. L.

Action of Sodium and of Hydroxylamine on Ethyl Cyanoacetate Phenylhydrazone and the Sythesis of Ethyl Cyanooxalacetate.

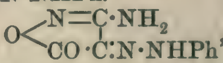
By Corrado Bertini (*Gazzetta*, 1901, **31**, i, 578—588).—The γ-phenylhydrazone of ethyl cyanoacetate (Weissbach, Abstr., 1898, i, 366), on treatment with aqueous alcoholic sodium hydroxide and subsequent precipitation with hydrochloride acid, behaves similarly to the β-compound (Krückeberg, Abstr., 1894, i, 369) in being transformed into the corresponding α-phenylhydrazine. In studying the further hydrolysing action of an alcoholic solution of sodium on these compounds, the author has hence confined himself to the α-derivative. When this compound is heated on the water-bath for an hour with an alcoholic solution of a molecular proportion of sodium, the addition of hydrochloric acid precipitates two substances:

(1) *Cyanoacetic acid phenylhydrazone*, $CO_2H\cdot C(CN){:}N\cdot NHPh$, crystallising from water in shining, yellow plates which melt at 157° and on further heating decompose with evolution of carbon dioxide. It is very soluble in alcohol, acetone, or acetic acid, and slightly so in benzene. A purer product is obtained, although in smaller yield, by using Weissbach's γ-phenylhydrazone in place of the α-compound.

(2) *Cyanoformaldehyde phenylhydrazone*, $CN\cdot CH{:}N\cdot NHPh$, which is obtained as sole product if a large excess of sodium is used in the reaction and the heating continued for a long time. It crystallises from water in long, slender, yellow needles melting at 162° and dissolves readily in alcohol, less so in boiling water, acetic acid, sodium hydroxide solution, or ammonium hydroxide, forming with the last-named a salt easily decomposed by heat. It forms silver, barium, copper, &c., salts. Its *nitroso*-compound, $C_8H_6ON_4$, crystallises from water in sparkling, yellow needles melting at 157—158°, and is soluble in alcohol or benzene and in alkali solutions, from which it is reprecipitated by acids; by double decomposition, copper, silver, barium, lead, &c., salts can be obtained. When hydrolysed with alcoholic potassium hydroxide, the phenylhydrazone yields large quantities of ammonia and a small proportion of a yellow substance which melts at 140°, and is probably the phenylhydrazone of glyoxylic acid already obtained by Elbers (Abstr., 1885, 535). With diazobenzene acetate, an aqueous solution of the sodium salt of cyanoformaldehyde phenylhydrazone forms azophenylformazylmethane (formazylazobenzene), $NHPh\cdot N{:}C(N{:}NPh)_2$.

The action of hydroxylamine on the α- or β-phenylhydrazone of ethyl cyanoacetate gives rise to two compounds: (1) A small quantity of a *substance* separating from water in yellowish-brown crystals melting at 162°; it has the composition $C_{11}H_{15}O_3N_3$ and is either an amide, $CONH_2\cdot C(CO_2Et){:}N\cdot NHPh$, or an oxime,

$$NOH{:}CH\cdot C(CO_2Et){:}N\cdot NHPh.$$

(2) *Aminoisooxyazolone phenylhydrazone*,  $O<\begin{array}{l}N{=}C\cdot NH_2\\ CO\cdot C{:}N\cdot NHPh\end{array}$, which is precipitated from its solution in ammonia by dilute acids in the form of a canary-yellow, voluminous precipitate; this deflagrates at 165° without melting and hence cannot be analysed; it gives barium, silver, copper, lead, &c., salts and a crystalline sodium salt very soluble in water; its *acetyl* derivative crystallises from a mixture of ethyl and amyl alcohols in shining, yellow plates which redden at 178—180°, and decompose with evolution of gas at 182°.

Ethyl cyano-oxalacetate, $CO_2Et\cdot CO\cdot CH(CN)\cdot CO_2Et$, is formed as sodium derivative when a mixture of ethyl oxalate and cyanoacetate in molecular proportion is gradually added to an absolute alcoholic solution of the corresponding quantity of sodium; it crystallises from ether or from a mixture of benzene and light petroleum in bundles of long, shining, silky-white needles melting at 98° and dissolves in alkali hydroxide solutions, from which it is precipitated by the addition of a mineral acid. Its alcoholic, but not its aqueous, solution is coloured an intense red by ferric chloride. When heated in ethereal solution with excess of phenylhydrazine, it yields the monophenylhydrazide of ethyl oxalate, $NHPh\cdot NH\cdot CO\cdot CO_2Et$. T. H. P.

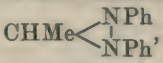
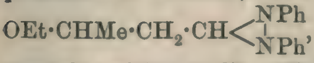
Phenylhydrazine Phenylcarbazinate. By PAUL FREUNDLER (*Bull. Soc. Chim.*, 1901, [iii], **25**, 859—862).—Phenylhydrazine phenylcarbazinate (see Fischer, Abstr., 1878, 307) is obtained in theoretical quantity by passing a current of carbon dioxide into a cold solution of phenylhydrazine in ether or benzene. When exposed to the air at the ordinary temperature it loses carbon dioxide and is converted into *phenylhydrazine hydrate*, $2N_2H_3Ph,H_2O$, which melts at 23—24°. Phenylhydrazine phenylcarbazinate melts and decomposes at about 80°, and is insoluble in ether or benzene but slightly soluble in water. Attempts to effect its dehydration, with the production of diphenylcarbazide, were unsuccessful. The properties of the phenylcarbazinate render it useful in the recovery of phenylhydrazine from solutions and in separating it from other bases, such as aniline, *o*-toluidine, and *p*-bromophenylhydrazine, which do not form analogous compounds. N. L.

Hydrazo-compounds. II. Action of Hydrazobenzenes on Aldehydes. By BERTHOLD RASSOW (*J. pr. Chem.*, 1901, [ii], **64**, 129—135. Compare following abstract).—Formaldehyde reacts readily with hydrazobenzene, producing, according to the conditions, either 1 : 2 : 4 : 5-tetraphenylhexahydro-1 : 2 : 4 : 5-tetrazine (m. p. 199°; compare Bischoff, Abstr., 1899, i, 279) or methylenebishydrazobenzene. Acetaldehyde and hydrazobenzene yield 3-methyl-1 : 2-diphenylhydrazimethylene and other similar compounds (*loc. cit.*). Other aldehydes with a normal carbon chain behave in an analogous manner, but heptaldehyde gives only a hexahydrotetrazine derivative.

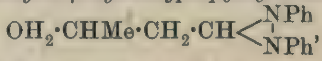
p-Dinitrohydrazobenzene and 2 : 4 : 6-hexanitrohydrazobenzene do not react with formaldehyde. On the other hand, *s*-phenyl-*p*-tolylhydrazine and the three hydrazotoluenes very readily yield hexahydrotetrazine and methylenebishydrazo-derivatives. With acetaldehyde, these hydrazo-compounds do not give hydrazimethylene derivatives, but dimethyltetratolylhexahydrotetrazines.

Dibenzylhydrazine reacts with still greater ease with aldehydes. K. J. P. O.

Action of Benzaldehyde and Aliphatic Aldehydes on Hydrazobenzene. By BERTHOLD RASSOW and MAX LUMMERZHEIM (*J. pr. Chem.*, 1901, ii, **64**, 136—165. Compare preceding abstract).—*Methylenebishydrazobenzene*, $CH_2(NPh{\cdot}NHPh)_2$, is obtained by mixing hydrazobenzene (2 mols.), dissolved in alcohol, with an aqueous solution of formaldehyde (1 mol.), and crystallises in plates melting at 145—146°. On warming the last-mentioned compound in alcoholic solution either alone or with formaldehyde, 1 : 2 : 4 : 5-tetraphenylhexahydro-1 : 2 : 4 : 5-tetrazine (m. p. 199°) is produced; with nitric acid, the latter gives a tetranitroazobenzene (m. p. 218°); by sulphuric acid, it is dissolved, forming a deep blue solution, and converted into benzidine.

1 : 2-*Diphenyl-3-methylhydrazimethylene*,  $\mathrm{CHMe}<\substack{\mathrm{NPh}\\ |\\ \mathrm{NPh}}$, prepared by the interaction of molecular quantities of acetaldehyde and hydrazobenzene, forms white crystals melting at 150—151°. By the action of excess of acetaldehyde (3 mols.) on hydrazobenzene (1 mol.) in the presence of alcohol, 1 : 2-*diphenyl-3-β-ethoxypropylhydrazimethylene*,  $\mathrm{OEt{\cdot}CHMe{\cdot}CH_2{\cdot}CH}<\substack{\mathrm{NPh}\\ |\\ \mathrm{NPh}}$, is formed; it crystallises in rhombic crystals melting at 67—68°, and is decomposed by dilute acids. When excess of acetaldehyde and hydrazobenzene react in the presence of

petroleum, 1 : 2-*diphenyl-3-β-hydroxypropylhydrazimethylene*,



$$OH_2\cdot CHMe\cdot CH_2\cdot CH\Big<\begin{matrix}NPh\\ |\\ NPh\end{matrix},$$

is obtained as crystals melting at 116—117°. In the presence of methyl alcohol, 1 : 2-*diphenyl-3-β-methoxypropylhydrazimethylene* is produced and crystallises in white needles melting at 81—82°; this methoxy-compound can also be prepared by heating the ethoxy-derivative with methyl alcohol at 120°.

The condensation product obtained by Cornelius and Homolka (Abstr., 1886, 1026) from benzaldehyde and hydrazobenzene, and thought by them to be triphenylhydrazimethylene (hydrazoin) is shown by the authors to be a mixture of azobenzene and benzaldehyde. K. J. P. O.

Addition of Aldehydoaminic Bases to Naphthols. II. By Mario Betti [with Cesare Speroni] (*Gazzetta*, 1901, **31**, ii, 191—200. Compare this vol., i, 81, 753).—The authors discuss the reactions taking place between benzaldehyde and benzylideneanil-β-naphthol and between β-naphthol, benzaldehyde, and aniline, which both yield the same product, namely, 1 : 2 : 3-triphenyl-4 : 2-β-naphtho*iso*oxazine (this vol., i, 611); with α-naphthol, the corresponding α-naphtho*iso*oxazine is obtained. The action of acetic acid on the benzylideneanilnaphthols yields the corresponding 1 : 2 : 3-triphenyl-4 : 2-naphtho*iso*oxazines.

Benzylidenephenylhydrazine-β-naphthol, $NHPh\cdot NH\cdot CHPh\cdot C_{10}H_6\cdot OH$, obtained by the action of phenylhydrazine on benzylideneanil-β-naphthol, crystallises from alcohol in small, white needles melting at 161°; it is readily decomposed by the action of cold dilute mineral acids, and with cold ferric chloride its benzene solution gives an intense violet coloration which disappears on adding excess of the ferric salt.

Benzylidenephenylhydrazine-α-naphthol crystallises from alcohol in white needles melting at 156°; with ferric chloride, it gives in the cold a transitory red coloration. T. H. P.

Action of Hypochlorous Acid on Diazobenzenesulphonic Acid. By Theodor Zincke (*Ber.*, 1901, **34**, 2853—2856).—Further researches to elucidate the constitution of the acid obtained (Abstr., 1896, i, 169) by the oxidation of *p*-diazobenzenesulphonic acid with hypochlorous acid. The oxidation of 6-diazo-*m*-xylene-4-sulphonic acid is shown to yield the corresponding azo-*m*-xylenedisulphonic acid, and therefore the acid described in the previous paper is 2 : 2′-dinitroazobenzene-4 : 4′-sulphonic acid, its formation being always accompanied by that of 4 : 6-dichloro-*o*-nitroaniline. This acid, when treated with hydrochloric acid, yields 2 : 2′ : 4 : 4′-*tetrachloroazobenzene*, which crystallises in small, slender needles melting at 161—162°, and when treated with hydrogen bromide gives 1 : 2 : 3 : 5-tetrabromobenzene. R. H. P.

Action of Diazobenzene on some Aliphatic Aldehydes and Ketones. By Eugen Bamberger and Jens Müller (*J. pr. Chem.*, [ii], **64**, 199—221).—A more detailed account of work already published (compare Abstr., 1893, i, 127, 182, 183).

Formazyl Methyl Ketone. By Eugen Bamberger and Paul de Gruyter (*J. pr. Chem.*, [ii], **64**, 222—244).—A more detailed account of work already published (compare Abstr., 1893, i, 157; 1894, i, 23, 98).

Formation of Ethyl Allophanate from the Azoimides of Hydroxy-acids. By THEODOR CURTIUS and C. MÜLLER (*Ber.*, 1901, 34, 2794—2799).—On diazotising the hydrazide of mandelic acid, an oily azoimide is obtained, which is highly unstable, and immediately undergoes hydrolysis: $OH\cdot CHPh\cdot CO\cdot N_3 + H_2O = Ph\cdot CHO + N_2 + NH_3 + CO_2$. When the diazotisation is incomplete, the benzaldehyde, formed by hydrolysis, condenses with unchanged hydrazide, producing benzylidenephenylglycollohydrazide, $CHPh(OH)\cdot CO\cdot NH\cdot N\colon CHPh$. With aniline, the azoimide reacts, forming mandelic anilide. On evaporation of a solution of the azoimide in alcohol-ether, phenylglycollourethane and ethyl allophanate are formed; the latter is either the result of the interaction of the urethane and azoimide: $OH\cdot CHPh\cdot NH\cdot CO_2Et + OH\cdot CHPh\cdot CO\cdot N_3 = 2Ph\cdot CHO + NH_2\cdot CO\cdot NH\cdot CO_2Et + N_2$, or of 2 mols. of the urethane: $2OH\cdot CHPh\cdot NH\cdot CO_2Et = EtOH + 2Ph\cdot CHO + NH_2\cdot CO\cdot NH\cdot CO_2Et$.

Only the azoimides of hydroxy-acids containing the secondary alcohol group, $CH\cdot OH$, yield ethyl allophanate with alcohol; thus glycollazide yields only glycolurethane, which is hydrolysed by strong acids to formaldehyde, ammonia, carbon dioxide and alcohol, whilst lactazide readily gives ethyl allophanate; from β-hydroxypropionazide, on the other hand, only a urethane is formed.

Phenylglycollohydrazide, $OH\cdot CHPh\cdot CO\cdot N_2H_3$, prepared from ethyl mandelate and hydrazine hydrate, crystallises in leaflets melting at 132° and dissolves in sulphuric acid with a transient blood-red colour; the *hydrochloride* is a crystalline powder melting at 149—150°; the *sodium* salt a yellowish-brown powder melting and decomposing between 215° and 220°.

Benzylidenephenylglycollohydrazide, formed when the components are mixed in aqueous solution, crystallises in needles melting at 149°. o-*Hydroxybenzylidenephenylglycollohydrazide*,

$$OH\cdot CHPh\cdot CO\cdot N_2H\colon CH\cdot C_6H_4\cdot OH,$$

forms needles melting at 179°; *cinnamylidenephenylglycollohydrazide*, $OH\cdot CHPh\cdot CO\cdot N_2H\colon CH\cdot CH\colon CHPh$, needles melting at 180°; *propylidenephenylglycollohydrazide* [*acetonephenylglycollohydrazide*],

$$OH\cdot CHPh\cdot CO\cdot N_2H\colon CMe_2,$$

leaflets melting at 134—135°. s-*Diphenylglycollohydrazide*,

$$N_2H_2(CO\cdot CHPh\cdot OH)_2,$$

is prepared by the action of iodine on phenylglycinohydrazide dissolved in alcohol, and crystallises in silky needles melting at 225°.

K. J. P. O.

Precipitation of Proteids by Anhydrous Sodium Sulphate. By S. N. PINKUS (*J. Physiol.*, 1901, 27, 57—65).—Anhydrous sodium sulphate possesses at 30° the same precipitating power of proteids as ammonium sulphate. It precipitates globulins at the point of half saturation (25 per cent.), and albumins at full saturation: it also allows of fractionation of proteoses. The proteid colour reactions are hardly at all interfered with; the nitrogen of the precipitate can be estimated directly: it is easy to obtain solutions containing only 5 per cent. of salt, and the salt itself is practically non-toxic. By adding to proteid solutions enough of the salt to absorb all the water, a product is obtained which can be preserved without change in the proteid. These are some of the advantages of the method. W. D. H.

Decomposition of Albumin. By MAXIMILIANO DENNSTEDT (*Chem. Zeit.*, 1901, **25**, 814—815).—In opposition to Kossel (this vol., i, 107), the author insists on the absolute necessity for the analysis of every form of proteid and also of all intermediate decomposition products. The drying of proteid substances should be accomplished in a desiccator over phosphoric oxide or in an oven at 100°, not at 110—120°, since combined water is driven off at this temperature. J. J. S.

Formation of Carbamide by the Oxidation of Albumin. By FRIEDRICH N. SCHULZ (*Zeit. physiol. Chem.*, 1901, **33**, 363—369 Compare Jolles, this vol., i, 490).—Jolles' method is criticised, especially from the point of view that it is impossible to remove all the salt by precipitation with alcohol, even when the operation is repeated 7 to 8 times. It is found that the carbamide oxalate obtained after such treatment may yield as much as 10 per cent. of ash. J. J. S.

Formation of an Isatin Derivative from Albumin. By JULIUS GNEZDA (*Compt. rend.*, 1901, **133**, 517—518).—When peptone is boiled with hypochlorous acid solution, it yields a very small quantity of a substance which seems to be identical with chloroisatin and has none of the properties of indole derivatives (compare Abstr., 1899, ii, 715).
C. H. B.

A Chlorinated Casein and its Decomposition Products with Fuming Hydrochloric Acid. By THEODOR PANZER (*Zeit. physiol. Chem.*, 1901, **33**, 131—150. Compare Habermann and Ehrenfeld, this vol., i, 622).—A chlorocasein obtained by the action of nascent chlorine (from hydrochloric acid and potassium chlorate) on casein has the following percentage composition: C, 47·05; H, 5·52; N, 12·40; S, 0·32; Cl, 8·32; P, 0·81; O, 25·67. It dissolves in dilute alkalis, but the solutions obtained have an acid reaction and are also capable of liberating carbon dioxide from carbonates. Salts of heavy metals yield precipitates, but the ordinary reagents for alkaloids, with the exception of potassium bismuth iodide, do not give precipitates with the substance.

For the preparation of the potassium derivative, 459 parts by weight of chlorocasein are required for every equivalent of the metal, for the silver derivative, 234·2 and for the copper, 463·4 parts by weight.

Among the products of the action of concentrated hydrochloric acid on this chlorocasein are chlorinated acids free from nitrogen, chlorinated nitrogenous humic acid, glutamic acid, leucine, and phosphoric acid. The presence of the following substances has been established: aspartic acid, arginine, histidine, and lysine, but not tyrosine. It is probable that the chlorine replaces amino-groups, hydrogen atoms, and possibly certain hydroxyl groups in the casein molecule. J. J. S.

Hydrolysis of Casein by means of Hydrochloric Acid. By EMIL FISCHER (*Zeit. physiol. Chem.*, 1901, **33**, 151—176. Compare Cohn, Abstr., 1896, i, 658; 1898, i, 343; 1899, i, 315; 1900, i, 466).—The method previously described (this vol., i, 192) has been employed for the separation of the amino-acids formed by the hydrolysis of casein with hydrochloric acid. In addition to the products obtained by others, the presence of the following amino-acids has been established—aminovaleric acid, phenylalanine, pyrrolidine-2-carboxylic acid, and probably glycine. These amino-acids are partially racemised by the esterification process and to isolate them it is advisable to completely racemise them by heating with baryta water under pressure and then to combine them with phenylcarbimide.

Aminovaleric acid phenylcarbimide crystallises from 50 per cent. alcohol in hexagonal plates melting and decomposing at 157—158° and yields an *anhydride*, $C_{12}H_{14}O_2N_2$, melting at 117°. l-*Pyrrolidine-2-carboxylic acid* is also present in addition to the racemic acid. It melts and decomposes at 203—206°, and at 20° has $[\alpha]_D - 77{\cdot}40°$ in aqueous solution, $[\alpha]_D - 46{\cdot}53$ in 20 per cent. hydrochloric acid solution and $[\alpha]_D - 83{\cdot}48$ in potassium hydroxide solution; its *phenylcarbimide* derivative, which was only obtained in the form of a resin, yields an *anhydride*, $C_{12}H_{12}O_2N_2$, crystallising in small prisms or flat needles melting at 144° (corr.). The copper salts of some of these amino-acids vary in solubility with the presence or absence of other amino-acids; for example, copper aminovalerate becomes soluble in absolute alcohol when *l*-pyrrolidine-2-carboxylic acid is present, and copper leucine and copper aminovalerate crystallise together in large prisms readily soluble in water and apparently form a molecular compound. The ester from phenylalanine is readily separated from the esters of glutamic and aspartic acids, which have approximately the same boiling points, by treatment with water. J. J. S.

A Hydrolytic Product from Edestin, its Relationship to Weyl's Albuminate and to the Histone Group. By THOMAS B. OSBORNE (*Zeit. physiol. Chem.*, 1901, **33**, 225—239. Compare Weyl, *ibid.*, 1877, **1**, 72).—Water and dilute acids transform edestin into a substance—*edestan*—insoluble in sodium chloride solutions of medium strength and identical with Weyl's albuminate. It is a true hydrolytic product and is probably the first substance formed in the hydrolysis of edestin to acid albumin. The percentage composition is practically the same as that of edestin; it forms salts with hydrochloric acid which are strongly acid to phenolphthalein. Edestan is insoluble in water or dilute ammonia and less soluble than edestin in potassium hydroxide solution. It gives most of the reactions which are characteristic of histones (Bang, Abstr., 1899, i, 836) although it appears to have little in common with true histones. J. J. S.

The Basic Nature of the Proteid Molecule and the Behaviour of Edestin to Known Quantities of Acid and Alkali. By THOMAS B. OSBORNE (*Zeit. physiol. Chem.*, 1901, **33**, 240—292).—The proteids are basic substances and form true salts with acids. The usual proteid preparations, which are either neutral or acidic to litmus, are really proteid salts. The free bases are best obtained by adding sodium or potassium hydroxide until the product is neutral to phenolphthalein. Preparations of edestin consist essentially of chloride when crystallised from sodium chloride, and of sulphate when crystallised from ammonium sulphate; when crystallised from a mixed medium, the salt formed is that with the negative ion which is present in largest quantity.

Water separates ordinary edestin chloride into a soluble part, *edestin dichloride*, and an insoluble part, the *monochloride*, both salts being isomorphous with edestin itself. To completely dissolve edestin, slightly more than the theoretical amount of hydrochloric acid, calculated on the assumption that 1 mol. of the base (mol. wt. 14500) combines with 2 mols. of the acid, is required, since a certain amount of hydrolytic dissociation occurs. The sulphates are less soluble than the chlorides and so far have not been obtained pure. Phosphoric acid behaves as a monobasic acid towards edestin and for the complete solution of edestin in either this acid or in acetic acid only slightly more than the theoretical amount of acid is required. *Edestin dinitrate* is much more soluble in pure water at 30° than at 20°.

Edestin also dissolves in alkalis; with sodium or potassium hydroxide, complete solution occurs when alkali and proteid are present in mol. proportion; with ammonia or sodium carbonate, however, a considerable excess of the alkali is required. The solutions in sodium or potassium hydroxide become cloudy when kept, probably owing to hydrolysis. The solubilities of edestin in water and in neutral sodium chloride solution are those of a globulin. Edestin monochloride, although insoluble in water, dissolves in saline solutions; the dichloride and sodium and potassium edestin are soluble in water or concentrated saline solutions, but insoluble in very dilute saline solutions. J. J. S.

Behaviour of Oxyhæmoglobin, Carbon Monoxide Hæmoglobin, Methæmoglobin, and certain of their Derivatives in the Magnetic Field, with a Preliminary Note on the Electrolysis of the Hæmoglobin Compounds. By ARTHUR GAMGEE (*Proc. Roy. Soc.*, 1901, **68**, 503—512).—Oxyhæmoglobin, carbon monoxide hæmoglobin, and methæmoglobin are found to be decidedly diamagnetic, whilst the iron-containing derivatives, hæmatin and acethæmin, are very strongly magnetic. The electrolysis of solutions of oxyhæmoglobin and carbon monoxide hæmoglobin shows that very probably the iron-containing group is (or is part of) an electronegative radicle; the iron in such a group generally exhibits diamagnetic properties. J. C. P.

Arnold's Neutral Hæmatin. By K. H. L. VAN KLAVEREN (*Zeit. physiol. Chem.*, 1901, **33**, 293—309. Compare Arnold, Abstr., 1900, i, 318; Formánek, *ibid.*, 532).—Arnold's neutral hæmatin is a proteid, differing in composition only slightly from hæmoglobin, the main difference being a lower percentage of iron. It is not a true hæmatin and for it the author suggests the name kathæmoglobin; the pure compound is best obtained by treating a concentrated solution of hæmoglobin crystals with 96 per cent. alcohol and saturated potassium hydroxide solution, warming to 60°, immediately neutralising, filtering, and pouring into distilled water; it may be purified by solution in 60 per cent. alcoholic sodium chloride solution and precipitation with water. On treatment with very dilute hydrochloric acid, kathæmoglobin, like oxyhæmoglobin, is converted into a hæmatin and a globin. The hæmatin from kathæmoglobin contains less iron than that from oxyhæmoglobin; and thus the name hæmatin comprises a group of compounds which differ from one another, but which probably contain a nucleus in common. J. J. S.

Hæmocyanin. By MARTIN HENZE (*Zeit. physiol. Chem.*, 1901, 33, 370—384).—Hæmocyanin was separated in a crystalline form from the blood of the octopus by the method introduced by Hopkins and Pinkus for crystallising proteids. It is not precipitated from its solutions by dialysis, nor can it readily be "salted out"; it is, therefore, not a globulin, as Halliburton considered. It is coagulated by heat at 68—72°. Its elementary composition is C, 53·66; H, 7·33; N, 16·09; S, 0·86; Cu, 0·38; O, 21·67 per cent. It gives the biuret (red-violet) reaction without the addition of copper sulphate. It is regarded as a copper albuminate, in which the copper is loosely combined, and can be readily split off by hydrochloric acid. One hundred c.c. of octopus blood yield 3·4 c.c. of oxygen, and 9 per cent. of hæmocyanin. One gram of hæmocyanin, therefore, combines with 0·4 c.c. of oxygen; that is about one-fourth of that held by hæmoglobin. W. D. H.

Fibroin from Silk. By EMIL FISCHER and ALADAR SKITA (*Zeit. physiol. Chem.*, 1901, 33, 177—192. Compare Weyl, Abstr., 1888, 857; Wetzel, *ibid.*, 1899, i, 466).—Among the products obtained from silk fibroin by hydrolysis with hydrochloric acid are *l*-tyrosine, 10 per cent.; *d*-alanine, 21 (Abstr., 1899, ii, 888); *l*-phenylalanine, 1—1·5; *l*-leucine, 1—1·5; glycine, 36, and other amino-acids. The method adopted for the separation of the acids was that previously described (this vol., i, 192). The *d*-alanine corresponds in configuration with *d*-lactic acid. J. J. S.

Decomposition Products of Proteids. By EDWIN HART (*Zeit. physiol. Chem.*, 1901, 33, 347—362. Compare Kossel and Kutscher this vol., i, 107).—The heteroalbumose and protoalbumose, obtained when santonin is digested with pepsin, differ in the amounts of hexon bases they yield. The heteroalbumose contains less histidine, but is richer in arginine than the protoalbumose. The heteroalbumoses obtained by coagulation and by precipitation with alcohol are apparently identical.

The amounts of ammonia and lysine produced on the hydrolysis of casein or glue with boiling acids are greater when mineral salts, for example, sodium chloride or sulphate, are present during the hydrolysis. The humin formed by the acid hydrolysis of glue in the presence of sodium chloride is free from nitrogen, and that obtained from casein yields no lysine on hydrolysis with sulphuric acid in the presence of sodium chloride. Zein, even in the presence of sodium chloride, yields no lysine. J. J. S.

A Crystalline [Peptone-Serum Product] ("Immunisierungsprodukt"). By HANS BUCHNER and L. GERET (*Chem. Centr.*, 1901, ii, 704; from *Münch. med. Woch.*, 48, 1163—1164).—When the serum from rabbits which have been treated with peptone or with ox blood is added to a solution of pure peptone prepared by Kühne's method, a precipitate is formed which consists of globulites or spherical masses of crystalline material arranged in concentric layers. The globulites are strongly refractive, and insoluble in hot nitric or hydrochloric acid, or in cold sulphuric acid, acetic acid, alcohol, or pepsin-hydrochloric acid, but dissolve in hot sulphuric acid; they give an intense coloration with iodine, but neither show Millon's nor the biuret reaction. When treated with ammonia, they swell to a slight extent, but much more with potassium hydroxide solution. On ignition, a residue of ash of precisely the same form is left; it probably consists of calcium compounds, for by the action of concentrated sulphuric acid on the globulites, calcium sulphate is formed. E. W. W.

A Ferment which Produces Mannitol. By Ulysse Gayon and Elisée Dubourg (*Ann. Inst. Pasteur*, 1901, **15**, 527—569).—A full description of the fermenting power of the enzyme producing mannitol from lævulose, which has been described by the authors (*ibid.*, 1894, **8**, 108). The enzyme ferments hexoses, pentoses, and saccharoses (without previous hydrolysis), forming carbon dioxide, acetic, lactic, and succinic acids and glycerol; mannitol is formed only in the case of lævulose, ethyl alcohol being obtained from other sugars. It is noteworthy that the sugars not fermented by yeast are decomposed by the mannitol ferment. The enzyme thus affords a means of detecting lævulose in mixtures of fermentable carbohydrates. R. H. P.

Oxydase and Peroxydase Reactions. By F. W. T. Hunger (*Chem. Centr.*, 1901, ii, 648; from *Ber. deutsch. Bot. Ges.*, **19**, 374—377). —The detection of oxidising enzymes by the guaiacum-hydrogen peroxide reaction is frequently interfered with not only by tannins but also by other substances. The milk from young cocoanuts, for instance, contains a sugar (not sucrose) which completely inhibits the reaction, but the milk from older fruit gives the coloration, although rather indistinctly. A solution of the enzyme obtained by treating the milk with 95 per cent. alcohol and redissolving the precipitate shows the reaction very distinctly, but when dextrose is previously added to the solution, the test fails. The milk from very old fruit which has not germinated and in which the sugar is completely changed to fat shows the reaction satisfactorily. The reducing effect has also been proved in the case of the sugar cane oxydases and other reducing agents such as hydrogen sulphide, hydrocyanic acid, pyrogallol, hæmatoxylin and brazilin also interfere with the reaction. Dilute acids destroy the coloration but it is re-formed on addition of alkali. According to Raciborski, the growing points of plants give the most intense coloration and these have been found by Went to be absolutely devoid of dextrose. E. W. W.

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